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The ocean depths

Science is still commonly portrayed as an entirely objective study in which one advance forms the logical prelude to the next, and new discoveries in one field are quickly and fully applied for the advancement of others. It need hardly be said here that such a picture is far removed from reality: it is a commonplace that while some fields are intensively active others are strangely neglected. One such neglected field at the moment is oceanography: it is a curious paradox that although much is known of the remotest and most inhospitable lands of the earth and we are clearly on the very threshold of exploring space, we still know remarkably little of the dark ocean depths that literally lap our modern civilization. It has been said, with a good deal of justification, that we know more about the surface of the Moon than we do of the bottom of the sea. The capture of living Coelacanths, supposedly extinct for some fifty million years, is only one indication, though a particularly striking one, of the limits of our knowledge.

To say that surprisingly little has been done in oceanography, having regard to the intrinsic interest and importance of the subject, is not by any means to belittle what has already been achieved. Some of the world's most memorable voyages have been carried out wholly or partly for the advancement of oceanography. Familiar early examples are those of Edmond Halley, in the late seventeenth century, who at great hazard penetrated as far as latitude 52½° S, and of James Cook, nearly a century later, whose epic voyages of scientific exploration twice took him round the world. Much later, another great British expedition, that of the *Challenger* (1872–76), is generally regarded as having laid the foundations of modern oceanography: in the course of this some 70 000 miles were covered—still a record for a voyage of this kind—and the results fill fifty massive volumes that remain standard works of reference. More recently, the *Discovery* committee's vessels made great contributions to our knowledge of the Southern ocean. But oceanography has long been a truly international science, and all the great maritime nations have sponsored important expeditions. Among them, to name only a very few, are Nansen's remarkable Arctic voyage in the *Fram* (1893–96); the German *National* expedition of 1889, memorable for Hensen's classic researches on the distribution of the plankton; the *Belgica* (1897–99), the first to winter in the southern ice; the Carlsberg Foundation's *Dana* expedition (1928–30); the extensive magnetic surveys of the American ship *Carnegie*; and the Pacific surveys carried out by the Scripps Institute of Oceanography. Such voyages have been an important source of new knowledge, but by no means the only one: fishery research vessels, oceanographic institutes, marine biological stations, and surveying and cable-laying ships have all made, and are still making, their contributions.

That so little is still known, despite all these agencies, is partly a measure of the immensity of the problem. More than half the surface of the earth is covered by sea more than a thousand fathoms deep, and millions of square miles of ocean are three times deeper. Impressive though they are, these figures are less daunting than they appear at first sight. The progress of oceanography does not depend on exhaustively surveying these vast regions both horizontally and vertically, any more than the progress of geology depends on surveying every square mile of the earth's land surface. Important principles can certainly be established by concentrating effort on limited objectives: a major problem today is to determine the most rewarding fields of study. Moreover, the progress of other branches of science has immensely increased the speed with which certain kinds of measurement can be made and evaluated. To quote a single example: the echo-sounder makes it possible for a continuous recording of depth to be made from a moving vessel—an immense advantage over the making of individual measurements in deep water by means of line and sinker. Again, much progress has been made in taking core-samples of deep-ocean deposits, and there are now shipborne gravimeters and towed magnetometers.

But the unevenness of progress in science as a whole is particularly manifest in oceanography. Progress certainly depends on more observational and experimental work at sea, of a carefully planned kind, but it is no longer true that 'only those who brave its dangers Comprehend its mystery'; much basic work on marine physics can best be done in laboratories ashore. Indeed, preoccupation with major economic problems—such as those of the fishing industry—certainly seems to have led to a too direct approach in some branches of oceanography. There are now welcome indications that analytical, as well as observational, methods are receiving increasing attention and that observations are being made to test theories. Much progress has been made, for example, in the theory of the generation, transmission, and dissipation of waves. Such knowledge, properly applied, can be of great practical importance to both coastal engineers and ship designers, whose approach has hitherto been, of necessity, largely empirical. What is important is to maintain a proper balance. There is a risk that the need to spend large sums on operating an oceanographic ship at sea will lead to inadequate provision for working up the results. Work in ships is an essential feature of oceanography, but the subject involves more than this; a rational attack on its problems requires the interest of scientists of many kinds and the provision of laboratories on shore and of a great variety of equipment.

When appropriate, the laboratory approach to oceanographic problems is attractive in several respects. Firstly, important results can be expected from a relatively small expenditure. Secondly, there is no lack of possible applications of new knowledge of fundamental principles. So far as shipbuilding is concerned, it is already clear that theory can make important contributions to ensuring that hull design is appropriate to the wave conditions most prevalent on the vessel's intended run. The possibilities for fishery research are sufficiently indicated by the fact that although the seas cover 72 per cent of the globe they yield only 1 per cent of our food. Again, the meteorologist and the disposer of radioactive and other industrial waste are alike interested in the factors that govern deep-ocean currents. In the last connection, it is disturbing to learn that a flow of nearly one knot has been recorded for several days at a depth of 4000 m in the Atlantic; clearly there are dangers in assuming that material dumped even in great depths will stay there indefinitely. Thirty years ago the marine biologist H. Bigelow stressed that 'the biologist . . . must perforce take as keen an interest as do his physical confrères in the modern application of mathematics to ocean dynamics'. Another important consideration has already been touched on: more attention to basic problems may well indicate how the research vessel can be used to better advantage.

Physical oceanography has perhaps already made its greatest contribution to navigation at sea, in the sense that the increasing size and power of ships makes them better able to meet severe conditions. In this field we are unlikely to see again anything as far-reaching in effect as Franklin's chart of the Gulf Stream, by use of which the eastward journey across the Atlantic could be shortened by as much as two weeks, or Maury's famous wind and current charts of 1847–60. But Admiral Smyth, a founder of the Royal Geographical Society, was over-optimistic when, in 1854, he claimed that the combination of science and practical seamanship had already nearly reduced the elements to subjection; better understanding of winds and currents, tides and waves, can certainly still help the mariner.

Oceanography has always been characterized by fruitful international co-operation. Franklin's edict that, despite the War of Independence, Cook was not to be molested by American warships during his voyages of scientific exploration is a particularly striking reminder of this tradition. Today many international agencies exist to promote oceanographic research. They include the International Council for the Exploration of the Sea, the International Association of Physical Oceanography, the International Council of Scientific Unions, UNESCO, the International Atomic Energy Agency, the World Meteorological Organization, and the Food and Agricultural Organization of the United Nations. Such a multiplicity of agencies is welcome evidence of recognition of the implications of oceanographic research, and it is indisputable that for extensive oceanic surveys—such as are currently planned for the Indian Ocean—some means of widely sharing the cost and effort is essential. But there is a danger that preoccupation with big international projects, prompted at least partly by immediate practical needs, will be to the detriment of fundamental research by individuals and small national research groups, from which important results may be expected for comparatively modest expenditure.

It has been said that activity and progress in a subject are in direct proportion to the interest that the universities take in it; by this criterion the outlook for oceanography is bleak indeed. Thus Britain, with a maritime tradition second to none, has only a single professorship of oceanography; while some other countries may be better endowed, it is certainly true to say that professorships in oceanography are few and far between. Expenditure on fundamental research in oceanography is small in comparison with the practical issues at stake. It is very much to be hoped that as more funds become available the needs of the individual will be remembered as well as those of the big international expeditions.

The efficiency of a honeybee community

C. G. BUTLER

A community of honeybees is an integrated group, the members of which can distinguish other members from intruders. Individual bees can pass on detailed information about the nature and location of food sources; they will produce a new queen only when the old one is no longer satisfactory. These different functions are discussed and illustrated in this article; the discussion of queen rearing is made particularly appropriate by the recent discovery of the chemical nature of queen substance. The photographs are by Treat Davidson.

A few years ago G. D. Glynne-Jones [1] released about two hundred worker honeybees, taken at random from a large colony, in a small greenhouse. Within a couple of hours these bees formed a cluster in one corner of the roof, and a few of them began to feed at a dish of sugar syrup on one of the benches. These bees were each given a distinctive paint mark; it was found that only about a dozen bees were leaving the cluster to collect syrup, and that they carried it back to the cluster and shared it with their companions before returning to the dish for more. Only these few bees left the cluster and collected food during the next three days. Even though they had neither queen, comb, nor brood, the bees had formed a rudimentary colony, and the fact that only a few individuals collected food for the whole group indicated the establishment of a division of labour among its members. This division between household bees concerned, for example, with comb building (figure 10), and feeding the larvae and the queen (figures 3, 11, 12), and field bees who regularly leave the nest in search of food (figures 6–9), is well established in every honeybee community. Unfortunately the way in which this major division of labour between the worker bees is effected is still unknown.

Until recently, the simple system suggested thirty years ago by G. A. Rösch [2] seemed to give a reasonable explanation of the facts. He had reached the conclusion that every worker bee normally carries out each of a number of tasks in a regular sequence between birth and death, starting as a nurse bee feeding the older larvae, and ending as a forager. He supposed that the particular job of a worker at any given time depended on her age; the degree of activity of various glands was related to this, as their secretions were necessary for different tasks. The system would need some degree of flexibility to suit the special requirements of the colony at any given time: Rösch supposed that the length of time a bee spends on one kind of job varies.

This simple theory was shown to be inaccurate in 1952, when M. Lindauer [3] published the results of very detailed observations in which he had followed the activities of several individually marked workers throughout most of their lives. He found that there is no regular sequence of hive duties, and that a household bee does several different kinds of job every day. Indeed, he found that a worker bee's life can be divided into only three distinct periods, instead of the seven or eight that had previously been proposed. In the first two or three days of life, the only task a worker appears to have is to clean out cells before the queen lays in them again; during the second period, which usually lasts about two weeks, she wanders round the nest doing various jobs; and, in the last period of her life, from when she is about eighteen days old until she dies, when she is about four weeks old, she is concerned with nest defence and foraging. So, as J. B. Free and Y. Spencer-Booth [4] have also recently shown, a bee in summer normally spends the first eighteen days of her life working in the nest, followed by a further week or ten days as a field bee.

According to Lindauer, about two-thirds of a household bee's time is spent either in resting or in patrolling the combs; he suggested that the significance of patrolling, which had been overlooked previously, might lie in the fact that it would enable each worker to find out what different jobs required attention, and that response to simple stimuli would result in each bee doing any work required. In support of this theory, Lindauer instanced examples of individual workers appearing to act quite independently of one another. For instance, when a larva is full-grown, a capping of wax is used to close its cell, but this is not made by a few bees only. On one occasion 657 visits, lasting nearly 6½ hours altogether, were

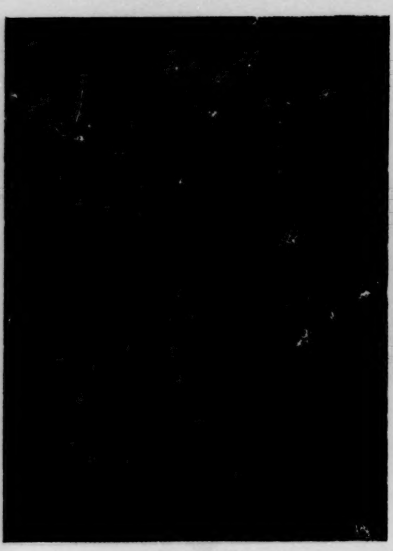


FIGURE 1 – *Swarm.*

FIGURE 2 – *Colony with nest in the open. Honeybees usually nest in dark cavities, such as hollows in trees.*

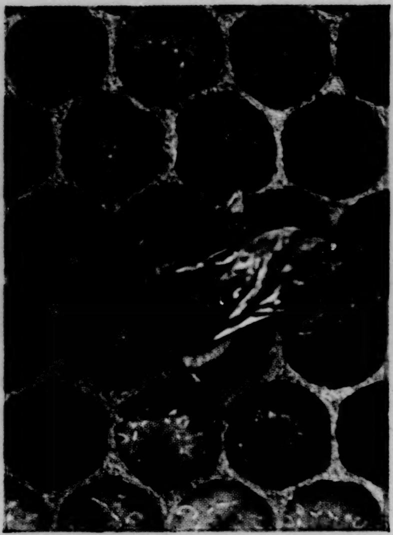


FIGURE 3 – *Nurse bee on brood comb, showing larvae and cell with egg.* (×3 *approx.*)

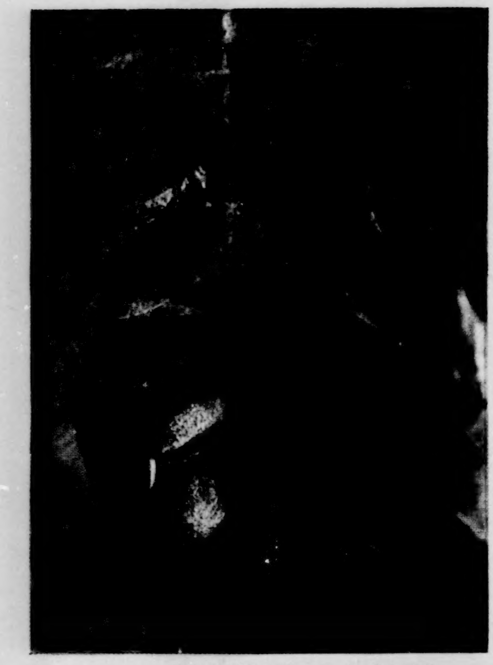
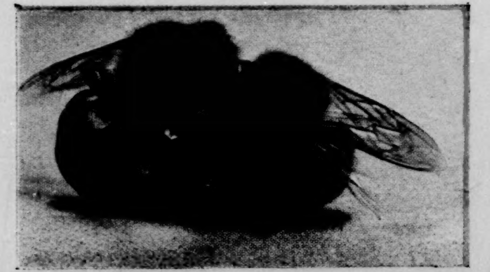


FIGURE 4 – *Underside of a worker's abdomen, showing wax scales.* (×11 *approx.*)

FIGURE 5 (*right*) – *Queens fighting.* (×2¼ *approx.*)



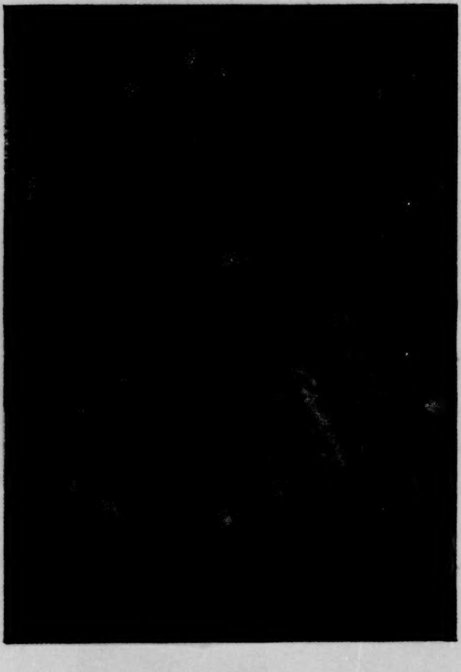


FIGURE 6 – *Tongue of nectar-seeking worker.* (×11 *approx.*)

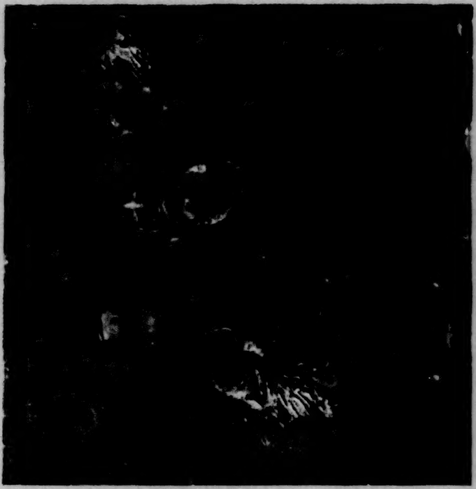


FIGURE 7 – *Workers on pollen-storage cells.* (× 1½ *approx.*)

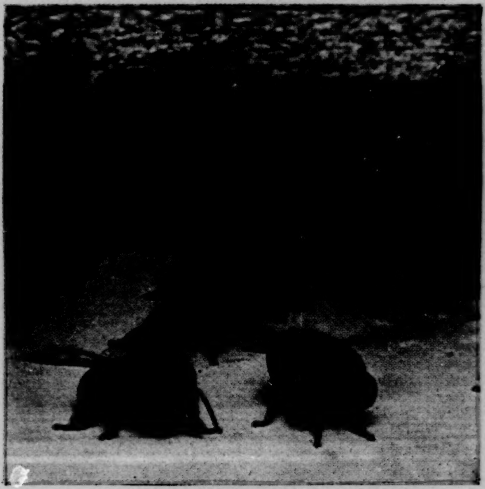


FIGURE 8 – *Forager (with pollen) and guards at hive entrance.* (×2 *approx.*)

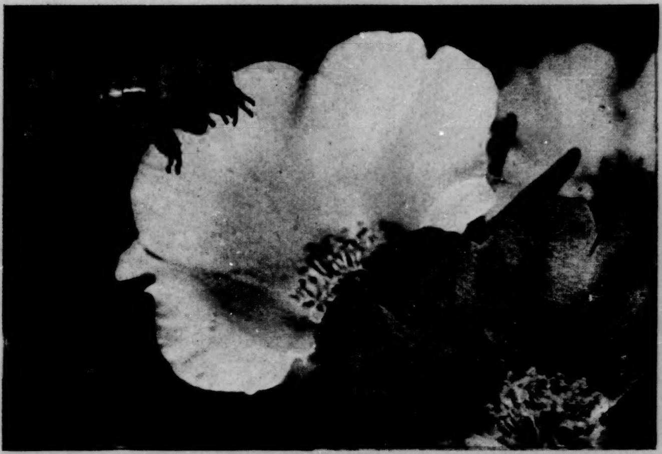


FIGURE 9 – *Forager approaching a flower, showing clumps of pollen on body and pollen-loads on hind-legs.* (×2 *approx.*)

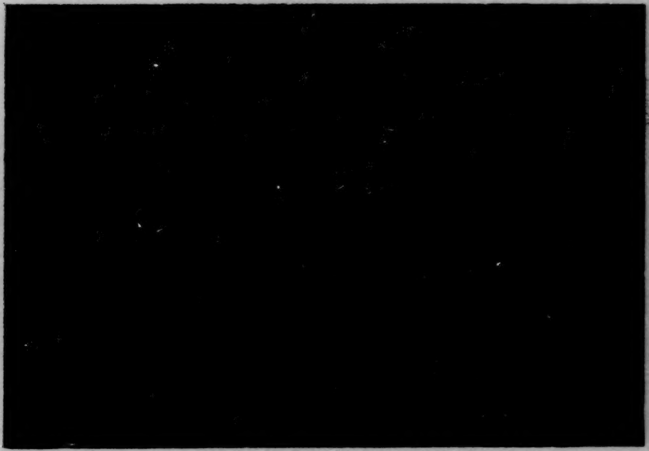


FIGURE 10 – *Comb building.*

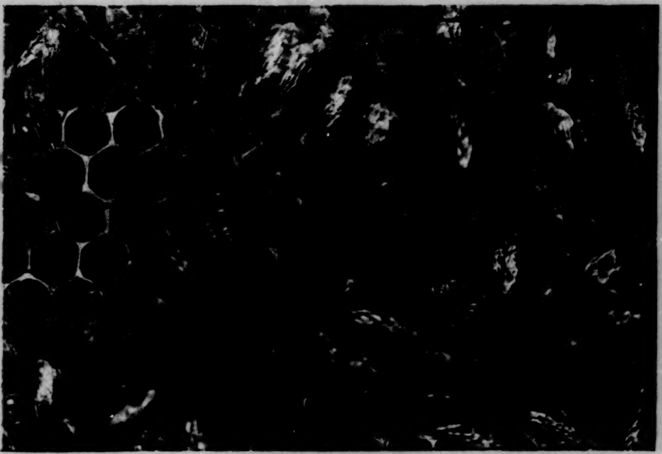


FIGURE 11 – *Marked queen (with a green spot) with 'court'. The worker near her tail is probably collecting queen substance, the one near her head is feeding her. (Natural size.)*

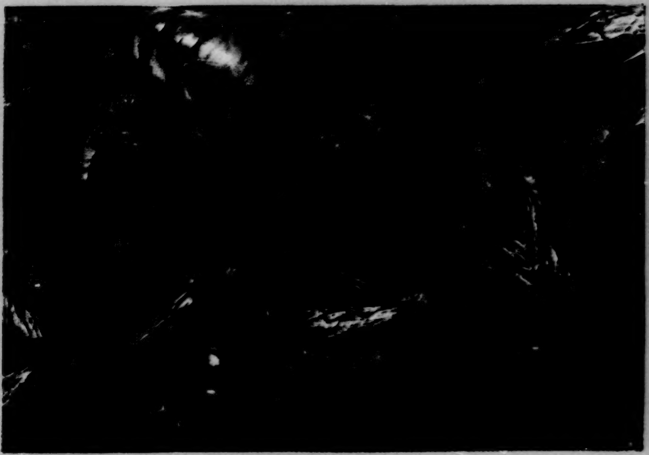


FIGURE 12 – *Queen with 'court', showing workers examining her with their antennae.* (×2½ *approx.*)

made by different bees before the capping of one cell was completed. Not only does such a job proceed in a haphazard manner, but sometimes a bee will remove a particle of wax that another bee has just laboriously added and use it in the capping of a neighbouring cell. A similar lack of co-operation is often seen among a group of guard bees dragging an intruder out of their nest. Each will often pull in a different direction [5].

It seems probable that Lindauer is correct, and that each bee reacts independently to the stimuli she receives from young and old larvae, intruding bees, half-capped cells, and so on. But it also seems probable that a bee spends more time doing those jobs for which she is best adapted at the moment. For instance, a bee whose wax glands are secreting wax abundantly (figure 4) may spend a lot of her time building combs.

It is difficult to see how the important division between household and field bees is effected. Perhaps, as C. R. Ribbands has suggested [6], converting nectar into honey, and comb building, done mainly by the older household bees, may be associated with an increasing tendency to leave the vicinity of the broodnest, this tendency eventually culminating in foraging.

Ribbands [7] showed that anaesthetization of young worker-bees with carbon dioxide causes them to begin foraging at an abnormally early age. O. Mackensen [8] found that queens that are prevented from mating seldom start laying eggs until they are about three weeks old, whereas similar queens, anaesthetized with carbon dioxide when about a week old, begin laying a few days later—at the same age as a queen that has mated normally. It seemed possible, therefore, that anaesthetization with carbon dioxide in some way aged the bees; however, Ribbands [7] found that this was not so, although it reduced the expectation of life of a worker by making her start the hazardous occupation of foraging at an abnormally early age. It may be that anaesthetization with carbon dioxide has a sudden effect on a bee's metabolism similar to one that perhaps occurs suddenly when a queen mates and starts egg laying, or more gradually when a worker forsakes household duties in favour of foraging.

It has already been mentioned that the average life of a worker bee in summer is about four weeks. However, those that are reared in autumn live much longer [4]. During early winter, fat and protein accumulate in a worker's fat-body, and A. Maurizio showed [9] that the long winter life appears to depend to some extent on this accumulation. Long-lived, 'winter', bees can be produced in summer in queenless colonies; the queenless bees accumulate fat and protein reserves.

Only bees reared in autumn survive into winter, and a critical period in a colony's life occurs in spring, when the old bees that have survived the winter are dying off rapidly and new ones are being reared. The death of many colonies early in some years may well have been caused by protein deficiency, because too little pollen was stored in the nests during the previous summer; the old bees probably died before enough young bees were reared to make the colonies viable.

Although the system of division of labour, in which a household bee wanders around the nest doing any job she finds, seems rather haphazard, it appears to be both efficient and sufficiently adaptable to allow even for sudden, extreme changes in a colony's requirements. When, for example, an experimental colony is made up entirely of foragers, some of them revert to brood-rearing and similar household tasks [10]; conversely, when one is made up entirely of young household bees, some begin foraging at an unusually early age [11, 12].

On leaving her nest for the first time, the average forager does not wander from one kind of flower to another searching for food. In fact very few bees ever leave the nest before being stimulated by the dance-language of successful foragers [3]. From this they learn that a certain kind of food, associated with a particular scent, is at a given distance and direction from the hive [13–17]. A small proportion of a colony's foragers leaves the nest without any knowledge of where there is food; these bees scout for the whole colony and are responsible for finding new sources as they occur. Unlike most foragers, who settle down to exploit a source thoroughly, scout bees tend only to visit a particular source a few times before they start looking for another [18]. When they are searching for new sources of food, scout bees are attracted by small, brightly coloured—especially blue and yellow—objects, such as flowers or even discs of paper. They seldom settle on them, however, unless the objects have a scent [19]. When a scout bee is attracted to a flower by its colour she hovers over it and, as soon as she perceives its scent, settles on it and extends her tongue to search for nectar in any narrow crevices (figure 6). If she finds plenty of food she collects a load before returning to her nest, where, by means of the 'dance-language' [13–17], she informs other bees of its whereabouts and recruits some of them to exploit the source.

On finding a rich source of food, a bee often exposes her scent-producing gland. Scent dispersed in this way helps searching foragers to find the food, and there is evidence that, although the scent is attractive to all bees, it is particularly attractive to other members of the scent-dispersing bee's colony [20, 21]. H. Kalmus and C. R. Ribbands [21] demonstrated that such differential attraction is a consequence of odour differences, and that every colony of honeybees possesses its own particular odour, shared by all its members and differing from that of other colonies. They found that the odour of a colony depends on the kind of food its members have been sharing among themselves. Different colonies, even in the same apiary, collect different proportions of their food from the various kinds of flowers available at any given time. If this explanation of the origin of distinctive colony-odours is correct, it follows that a number of colonies compelled to share a single source of food should all acquire the same odour. Ribbands [6] obtained striking confirmation of this by removing the stores of food from a number of colonies and taking the colonies to a heather moor where the only source of food was *Calluna vulgaris*. At the end of two months all the colonies had, apparently, a common odour, as their members could be freely interchanged.

Colony odour plays an important role in enabling bees that are guarding the entrance of their nest against intruders to distinguish between their own sisters and bees from other colonies [22, 23]. But although the workers of a colony share a common odour, the queen does not appear to share the same odour as the workers; these seem to be unable to distinguish between their own mated or virgin queen and similar queens from other colonies introduced into their nests; if they can make the distinction, they ignore such differences [24]. Nevertheless, worker bees certainly distinguish between mated and virgin queens by their different odours [25], and are attracted towards a queen, even one that has been dead for several months, by her body odour [26].

Queen odour also probably helps a queen to find a rival that has appeared in her nest and so gives her an opportunity to destroy her (figure 5), unless the workers prevent the two queens from meeting. It also seems possible that the worker bees in a swarm (figure 1) are aware that their queen has swarmed with them by an odour from her body. Certainly if she fails to leave the nest with them or to join them when they cluster, the workers soon notice her absence and return to their old nest.

When worker bees lose their queen they try either to rear a new one or, sometimes, to join a group of bees that has one. Generally speaking, the presence of a laying queen in a colony suffices to inhibit both development of the workers' ovaries and queen rearing by them. Such inhibition is not brought about by the bees realizing that their queen is in the nest because of her pervading odour. In fact the sight, sound, and scent of a queen do not cause such inhibition, which only occurs when some members of the colony make frequent contact with their queen [27–30]. This led the author [29] to suggest that some of the members of a honeybee colony obtain something—queen substance—from their queen that they share with other members of their colony and that, when each bee receives enough, inhibits development of the ovaries and queen rearing by the bees. Experiments in which small groups of workers were allowed access only to limited parts of the bodies of their queens for two or three days but remained inhibited from queen rearing indicated that this substance is present all over a queen's body [29]. This queen substance could also be recovered from the crops of worker bees caught while licking their queen (figure 11); it is almost certainly shared among all the members of a colony in regurgitated food [31].

Many experiments indicated a quantitative relationship between the amount of queen substance and the inhibition of queen rearing. However, although much circumstantial evidence in favour of the existence of queen substance accumulated, it was not until 1957, when a quick and fairly sensitive method of bioassay was developed, that it became possible to show that an extract in ethanol of a substance from a mated queen's body, when fed to queenless worker bees, inhibits them from building queen cells [32].

Having established the existence of queen substance, one of the next problems was to discover its source. The fact that the mandibular glands of a queen are proportionally very much larger than those of a worker led C. G. Butler and J. Simpson [33] to seek and find queen substance in them, and to suggest that the queen distributes it over her body during grooming.

Under natural conditions new queens are generally reared to replace old ones either by supersedure or swarming. (Supersedure differs from swarming in that the colony replaces its queen with a young one without forming a new colony.) Many theories have been suggested to explain both supersedure and swarming: there is now no doubt that in connection with both, queen rearing happens because the workers receive too little queen substance [35]. With swarming, this seems to be brought about in two ways. Firstly, when a colony is overcrowded, the workers get too little queen substance, even though the queen produces plenty in her mandibular glands, either because the bees who normally lick it from the queen's body are unable to do so properly in the crowded conditions, and are unable to distribute what they do collect widely enough, or, possibly, because the queen is jostled around so much that she is hindered in grooming, and hence in distributing queen substance over her body. Secondly, when a colony that is not overcrowded builds queen cells preparatory to swarming, its queen is actually producing too little queen substance. Both queens that have been superseded and those that have accompanied swarms from uncrowded colonies contain less than one-quarter the amount of queen substance of an average, mated, laying, queen, whereas queens of swarms from overcrowded colonies have just as much [35].

Queen substance has now been isolated, by R. K. Callow, and N. C. Johnston, as waxy crystals, 0·13 µg of which will inhibit a worker from queen rearing for at least twenty-four hours [36]. This crystalline material has been identified by these workers as 9-oxodec-2-enoic acid,

$$CH_3.CO[CH_2]_5.CH:CH.COOH,$$

synthesized and shown to be biologically active [37].

To sum up, the efficiency of a honeybee community (figure 2) owes much to (*a*) a division of labour, not only between the queen and the thousands of workers, but also among the workers themselves; (*b*) the attraction workers have for each other and the attraction of a queen for workers—which keep the colony together; (*c*) a system of communication between the workers by means of which detailed information is given about food sources; (*d*) a method by which workers can distinguish between members of their own colony and intruders from other colonies; this is essential to nest defence; (*e*) a system of control which prevents ovary development and queen rearing by workers so long as a satisfactory queen is present, but which allows the colony to replace its queen by a young one and also to reproduce itself by swarming when conditions are favourable.

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Beryllium

M. K. McQUILLAN and T. W. FARTHING

Beryllium has been known since the end of the eighteenth century and has for some time been used in copper alloys, but it is the development of atomic reactors that has made the preparation and working of the metal an important industrial process. The very low neutron cross section of the metal makes it valuable as a canning material for the fuel rods in gas-cooled reactors. The processing of the metal presents many unusual features, resulting from both the inherent physical properties of the metal and its high toxicity.

Beryl, the mineral which gives beryllium its name and which is still the only commercial source of the metal, has been known for thousands of years, both as a semi-precious gemstone and, in its green single-crystal form, as emerald. The history of the metal itself, however, is much shorter. It was isolated in 1798 by Vauquelin, but its debut as an industrial material occurred only about thirty years ago, when it was observed that small additions of beryllium to copper could give the latter the strength and elasticity which pure copper notoriously lacks but without destroying the high thermal and electrical conductivity upon which so many of the uses of copper depend.

Copper-beryllium alloys still account for about three-quarters of all beryllium extracted from its ores, but in the last fifteen years or so the pure metal has become of interest, because of its exceptional combination of properties, as a material for use in nuclear reactors. Without this development it is very probable that pure beryllium would still be little more than a metallurgical curiosity, although, as we shall see later, it has other possible applications.

From the point of view of a nuclear engineer, the most important single property of beryllium metal is its very low absorption of thermal neutrons—the lowest of any structural metal. Neutrons are the means by which nuclear reactions are propagated in reactors, and reactor efficiency thus depends on keeping adventitious neutron absorption and losses to a minimum. Neutron-absorption characteristics are therefore among the principal factors determining choice of reactor materials, and hence beryllium is naturally favoured in this respect. It has, moreover, a very low atomic weight, which fits it for use as the moderator, the material surrounding the fuel and serving to slow down the neutrons produced in the fission process so that they can more efficiently interact with further uranium nuclei.

Although the essential characteristic of beryllium, from the nuclear engineering point of view, is its low neutron-absorption it is also of interest to consider its general behaviour under neutron bombardment, as this will largely govern its behaviour in a reactor. When beryllium is bombarded with fast neutrons (about 2 MeV) the main nuclear reactions occurring are those producing helium and tritium (^3H):

1. (n, 2n) $^9Be + n \longrightarrow {}^8Be + 2n$ (200 millibarns[1])
$^8Be \longrightarrow 2\,{}^4He$

2. (n, α) $^9Be + n \longrightarrow {}^6He + {}^4He$ (50 millibarns)
$^6He \xrightarrow{\beta} {}^6Li$
$^6Li + n(\text{thermal}) \rightarrow {}^4He + {}^3H$ (950 barns)
$^3H \xrightarrow{\beta} {}^3He$

Irradiation experiments suggest that, at temperatures below 600° C, gases produced during neutron irradiation will not have any serious effect on the properties of beryllium.

Discovery of the promising nuclear properties of beryllium led American workers to undertake, in the period 1945–50, an intensive study of its technology, on the results of which a considerable part of present-day industrial practice has been based. Since then there has been some slackening of American interest in beryllium because the general trend of reactor design for power production in America has been towards a pressurized-water reactor operating at about 300° C, for which beryllium would have inadequate corrosion resistance. Now, however, a developing interest in new types of reactor—such as the so-called package reactors, which are intended to provide a flexible and transportable power source, and high-temperature forms of the gas-cooled reactor—is again bringing beryllium to the forefront of the American nuclear-energy programme.

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[1] The barn (10^{-24} cm^2) is the unit of neutron cross section.

In Britain, reactor design has taken a different course. The reactors favoured here for power production are graphite-moderated and gas-cooled, as typified by Calder Hall and its successors, and in such reactors beryllium can be expected to make an excellent sheathing (canning) material for the uranium fuel, as it is compatible both with the carbon dioxide coolant and with the graphite core into which the sheathed fuel is inserted. Interest in beryllium among British nuclear engineers has consequently been maintained, though the metal has not yet been used because so far operating temperatures have been such that the temperature at the surface of the fuel can has not exceeded 400–500° C, at which level more readily available materials, notably magnesium, can be used. At higher operating temperatures such as are proposed for a new type of experimental reactor, known as the Advanced Gas-cooled Reactor (AGR), the surface of the fuel can is expected to reach about 600° C, at which present canning materials will have insufficient strength and stability. They must therefore be replaced by material having greater high-temperature strength.

Higher operating temperatures will also involve a change in the nature of the fuel itself. When irradiated with neutrons, uranium swells and changes its shape. At the working temperature of Calder Hall and of the nuclear power stations now being built in Britain this is not a serious problem, but under the more exacting conditions of the AGR the swelling of the uranium would create much greater difficulties. For the AGR the fuel will, in fact, be uranium oxide, which has considerably better dimensional stability under irradiation. The proposed change in fuel, however, brings with it new problems, because uranium oxide suffers from the disadvantage of poor thermal conductivity: in order to provide sufficient cooling, the diameter of the individual fuel rods has to be appreciably decreased, thus increasing the proportion of sheathing to fuel in the core. In the new design, therefore, sheathing-material of low neutron-absorption is more important than ever. It is fortunate that in beryllium, which from this point of view is the obvious material to use, we have also a material of reasonably high melting point (1285° C as compared with 650° C for magnesium), which promises good high-temperature strength; thus two of the major problems of the AGR concerning constructional materials can be solved simultaneously. It has therefore been decided to use beryllium cans for the AGR, and in consequence industry is now for the first time dealing with the metal in quite large quantities. As we shall see, this is no easy task, for reasons connected with both metallurgy and with the health of the workers concerned.

PROPERTIES

Beryllium is a true metal, in that it has the electrical and thermal properties and the lustrous appearance by which metals are usually recognized. At the same time it has other characteristics which set it apart from the general run of metals and put difficulties in the way of its industrial use.

One of the most important of these is its behaviour on deformation. The malleability which allows metals to be worked into complex shapes is a consequence of their simple crystal-structure together with the absence of direct and specific bonds between one atom and the next. Under an applied force it is possible for atoms in one plane of a metal crystal to move with respect to those in an adjacent parallel plane[1] without disrupting the crystal, the sum of a large number of such atomic-scale movements making up a macroscopic shear. Naturally, different forces will be required to produce shear on different crystal planes. In normally malleable metals the shearing process occurs on one type of plane after another as the component of applied force, resolved in the appropriate direction of shear for each type of plane, exceeds the critical magnitude for the plane in question. The higher the degree of symmetry in the crystal lattice the greater the number of planes on which the shearing process (slip) can take place and the smaller the range of magnitude for the critical shear-stresses involved.

Beryllium has a crystal structure of the close-packed hexagonal type. Its axial ratio, however, is 1·568, which is too small for ideal close-packing; beryllium is not, therefore, among the metals having the highest degree of symmetry. Nevertheless, there is no *a priori* reason why a metal having such a crystal structure should not be fairly readily deformed by making use, for instance, of slip on the pyramidal $\{10\bar{1}1\}$ planes, as in titanium, which has a closely similar crystal structure and which can be very ductile indeed. Normal commercial beryllium, however, does not in fact deform in this way. Slip can occur on the basal (0001) plane and on the prismatic $\{10\bar{1}0\}$ planes, the slip directions being $\langle 11\bar{2}0\rangle$. Unfortunately at room temperature the critical resolved shear-stress for slip on the $\{10\bar{1}0\}$ planes is high compared with the stress needed to bring about cleavage fracture on the (0001) plane, and consequently cracking tends to occur before very much $\{10\bar{1}0\}$ slip takes place. In practice, therefore, room-temperature deformation is confined to slip on the (0001) plane, and forces applied in the majority of directions in the crystal will cause brittle fracture.

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[1] This process does not, of course, involve the movement of whole planes of atoms simultaneously—such a movement would require impracticably large forces—but is accomplished by the propagation through the crystal of imperfections in the lattice known as 'dislocations'.

This inconvenient behaviour on deformation means that the polycrystalline aggregate making up a normal piece of beryllium will not have sufficient ductility for engineering purposes unless special care is taken to ensure that the grain structure is such as to allow maximum advantage to be taken of the slip that can occur before fracture takes place. It is essentially a question of achieving a sufficiently small grain-size coupled with a suitable grain-orientation, and the technology of beryllium is considerably complicated by the requirements of grain-structure control.

Another characteristic of commercial beryllium that has considerably influenced the development of working procedures is the complex relationship between temperature and ductility, the form of which, as suggested by early work on beryllium [1], is illustrated in figure 1. A rather more detailed picture may be revealed by current investigations—indeed, it has already been shown by A. B. Brown, F. Morrow, and A. J. Martin [2] that suitably treated beryllium can have high ductility in the temperature region of about 600° C, where a minimum in the ductility/temperature curve is normally observed—but, at present, production practice is still governed very much by the need to work at a carefully controlled temperature in order that sufficient ductility can be reliably produced.

Beryllium has a number of other chemical and physical properties—some advantageous, some the reverse—which set it apart from the common run of metals. It is, for example, exceptionally light, having a density of only 1·85 g/cm^3, and it is certainly the lightest of potential structural materials. In beryllium, lightness is also coupled with quite high strength and—even more important—very great rigidity; its ultimate tensile stress ranges from 20 to 50 tons/in^2 at room temperature, and its modulus of elasticity (44×10^6 lb/in^2) is far above that of most other metals. The thermal conductivity of beryllium at room temperature (0·385 cal cm/cm^2 sec °C) is exceeded only by those of gold, silver, copper and aluminium, and its specific heat (0·425 cal/g °C) is also high.

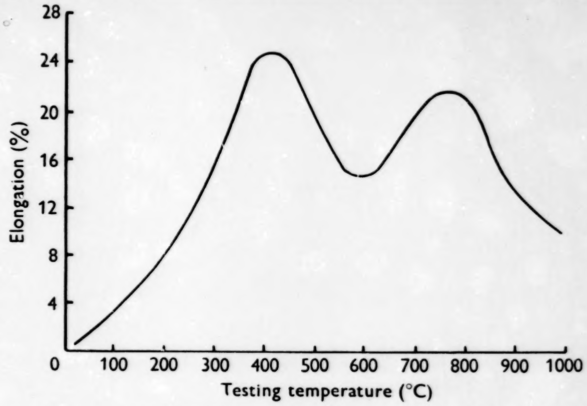

FIGURE 1 – *The effect of temperature on the ductility of polycrystalline beryllium as measured by elongation to fracture in short-time tensile test.*

Chemically, beryllium shows many similarities to aluminium. It is extremely reactive *per se*, but in air or oxidizing atmospheres at room temperature it forms a thin, adherent, impervious surface-film of inert oxide, which can protect the metal against certain types of chemical attack, giving it a spurious nobility. The protective characteristics of beryllium oxide (beryllia) are also evident in the resistance to tarnishing or oxidation shown by some beryllium-containing alloys. Silver, for instance, can be made appreciably more resistant to tarnishing by the addition of very small quantities of beryllium.

Beryllium dissolves rapidly in sulphuric and hydrochloric acids, but in nitric acid the rate of attack depends on acid concentration. Under some conditions the rate of attack by nitric acid falls to zero, the metal becoming passive. This is probably explained by the ease with which a protective coating of beryllia may be re-formed under oxidizing conditions. The corrosion of beryllium by neutral aqueous solutions is extremely variable, largely because of the important part played by very small quantities of impurities in the metal or the corroding medium, which cannot always be accurately controlled. For instance, the presence of a small amount of the ion of a more noble metal in the corrosive solution may give rise to pitting, as in the case of aluminium. As the quality of the metal available for research in the past has not been consistent, interpretation of the corrosion behaviour of beryllium is not always easy.

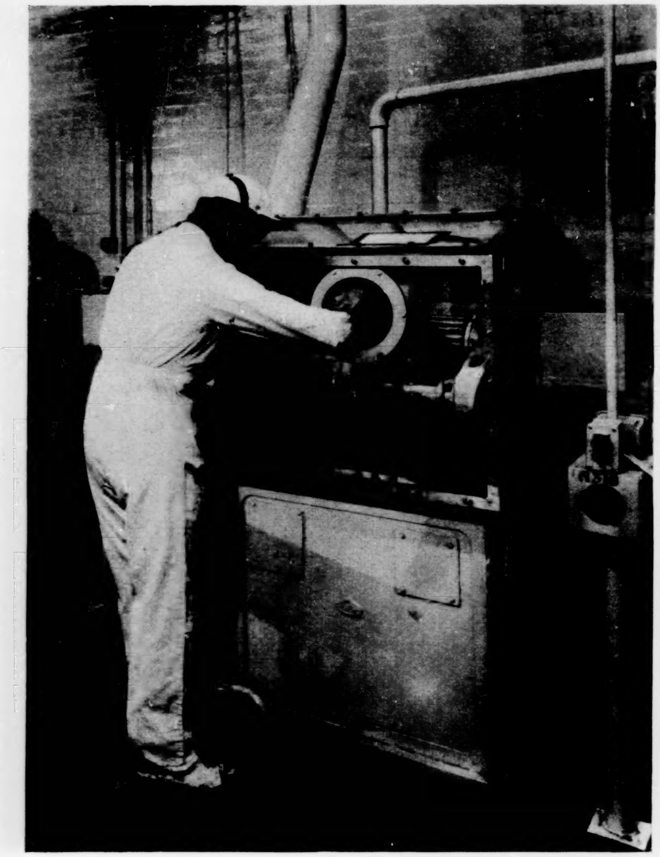

FIGURE 2 – *Components are being cut to length in a glove-box. Face masks are worn while equipment is being commissioned.*

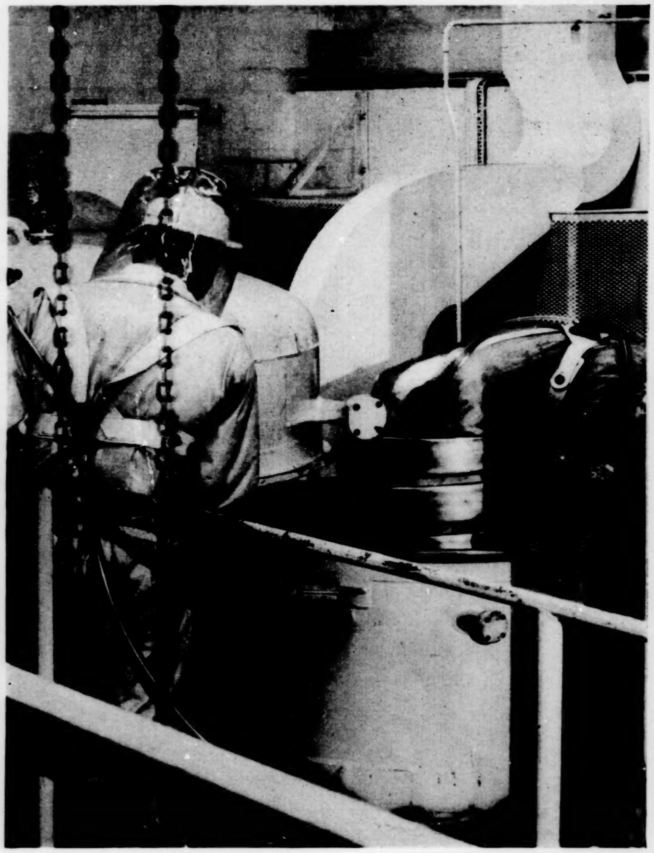

FIGURE 3 – *Maintenance staff working on a sintering furnace wear special protective clothing.* (*Figures 2 and 3 by courtesy of Metals Division of Imperial Chemical Industries Limited.*)

In the conditions foreseen for the AGR, that is, in carbon dioxide at 600° C, beryllium behaves satisfactorily as long as the gas is dry, but when water vapour is present the material is liable to suffer sudden marked increases in corrosion rate after a lapse of time. This phenomenon is known as 'breakaway', which graphically describes the often catastrophic effects of the change in the corrosion rate.

Above about 700–800° C, beryllium begins to react at an appreciable rate with air. For hot-working processes, therefore, some form of protection against oxidation must be provided, not only because it is difficult to work with a material which forms a heavy surface scale, but also because the dissemination of beryllium oxide in the atmosphere constitutes a severe health hazard. Molten beryllium is extremely reactive and will attack most materials with which it comes in contact; it can, however, be contained in crucibles made of beryllium oxide.

THE PROCESSING OF BERYLLIUM

Beryllium is extracted from beryl (beryllium aluminium silicate) by a process having four principal stages:

1. Separation of the beryllium content of the ore.
2. Conversion to beryllium hydroxide.
3. Production of a halide of beryllium.
4. Reduction of the halide to metal.

The separation stage involves treatment with fluoride or sulphate, producing a water-soluble beryllium salt from which the hydroxide is precipitated with alkali. The choice of the halide into which the hydroxide is then converted depends on the reduction method to be used. For reduction with magnesium, the method commonly used in the United States, the material required is beryllium fluoride, but for an alternative process, developed principally in France and involving electrolysis in a fused-salt bath, beryllium chloride is used. The two processes yield beryllium metal in different forms, magnesium reduction producing material described, from its appearance, as 'pebble', and the electrolytic method giving dendrites or flakes.

Neither reduction process gives 'raw metal' sufficiently pure for direct use; if processed without further purification the corrosion resistance of the product would be poor and very variable. It is necessary, therefore, to remove impurities—particularly residual volatile substances such as magnesium, sodium, and halides—in order to ensure a final product that has satisfactory corrosion-resistance and is uniform in its other properties. This is done by vacuum melting, usually in an induction furnace using a beryllia crucible; electric-arc melting has been used, but only on a very much smaller scale. The grain structure of the cast material is such that its room-temperature ductility is close to zero, and the room-temperature mechanical properties obtained after processing it are not as good as those of material produced from fine-grained starting stock. To achieve optimum properties, therefore, it is necessary to convert the ingot to fine powder, and consolidate it once more by one of several different techniques to produce fine-grained metal. Powdering is done first by turning the ingot to swarf and then grinding to 200 mesh. Ball mills are sometimes used, often with tungsten carbide balls to reduce iron contamination, but when contamination must be at a minimum the swarf is ground between beryllium plates in an attrition mill.

Methods available for consolidating the powder range from the old-established powder-metallurgy technique of cold pressing, followed by sintering, to the method known as pressureless sintering. This consists of pouring loose powder into a suitable die and consolidating it, without applying pressure, by heating it in vacuum at a temperature very little below the melting point. More efficient consolidation is achieved, however, by compressing the powder at elevated temperatures, thus combining the compacting and sintering operations, and though this puts very severe stress on the compacting tools and can be very time-consuming, it has become the most common procedure. The operation is done in vacuum at 1000–1100° C under an applied pressure which may be anything from about 50 lb/in^2 up to about 1 ton/in^2. The actual pressure is determined by such practical factors as the type of die material available and production economics. Hot pressing was first applied to beryllium in the United States, as an alternative to casting for producing large slabs of metals required for reflectors in an early materials-testing reactor. The method has since been developed there to a stage at which pieces of metal several inches thick and about 10 ft^2 in area can be made on a regular production basis. Cylinders about 4 or 5 ft in diameter and the same in height, and other shapes weighing up to 2000 lb, are also being successfully manufactured.

Even in the fine-grained condition, beryllium has insufficient ductility at room temperature (about 3–5 per cent elongation) to make cold working practicable, but further fabrication can be carried out by extrusion, rolling, forging, and other normal working techniques at temperatures sufficiently high to bring the prismatic $\{10\bar{1}0\}$ slip planes into operation. In practice, working temperatures range from 400° C upwards. At 400° C advantage can be taken of the first peak on the ductility/temperature curve; the maximum working temperature is usually 1000–1050° C.

During mechanical working the beryllium crystals tend to arrange themselves in such a way with respect to the direction of working that slip occurs easily in this direction. In normal wrought beryllium, which is most commonly produced by extrusion, ductilities of up to 30 per cent can be expected in the longitudinal direction. Elongations as high as 50 per cent in the rolling direction have been obtained in specially prepared sheet, but in directions other than the rolling direction much lower ductilities are exhibited. When there are two working directions, as for example in cross-rolling, high elongations can occur in both directions, but the ductility in the direction perpendicular to the plane of the sheet is again very low.

THE TOXICITY OF BERYLLIUM

One of the most important points to be taken into account in processing beryllium is that it is highly toxic. This manifests itself in two main forms—an acute irritation of the respiratory tract, including chemical pneumonia, and a chronic disease of the lungs, now known as berylliosis. Like many other metals, beryllium may also cause skin reactions such as dermatitis and ulcers, particularly if it finds its way into an open wound, though compared with the effects on the lungs this is of less importance. Various views have been expressed on the relative toxicities of different beryllium compounds, but from the health point of view, all compounds must be regarded as suspect. Much still remains to be learned of berylliosis, but it is becoming clear that only relatively few people are susceptible to it: it appears to have aspects akin to those of an allergy. A very disconcerting feature of the disease is that its onset may be delayed until many years after the last time at which the victim was exposed to beryllium.

In working with the metal or its compounds, the danger arises not from the solid material, which can be handled quite safely at room temperature, but from breathing finely divided material, which might be retained in the lungs: the beryllium content of the working atmosphere must therefore be strictly controlled. Work done in the United States, where the beryllium hazard was first recognized in the early 1940s, has produced recommendations for tolerable (extremely low) atmospheric levels that are internationally accepted. Within the plant, the atmospheric concentration, averaged over an 8-hour working shift, should not exceed 2 $\mu g/m^3$. Further, no matter how low the shift average, no worker must at any time be exposed to an atmospheric concentration of more than 25 $\mu g/m^3$. In the neighbourhood of a plant the atmospheric level, averaged over a month, must be less than 0·01 $\mu g/m^3$.

In order to keep within these very stringent safety-limits, a number of precautions must be taken. The difficulty is enhanced not only by the fact that powdering is an intrinsic part of the processing, but also by the brittleness of the metal. This, aggravated by the need to work without a lubricant in order to prevent contamination, results in the formation of much finely divided material during machining. Machine tools and other equipment are therefore set up in individual enclosures, from which the air is continuously pumped (figure 2). Handling is done with rubber gauntlets let into the sides of the enclosure. Special clothing is worn by all who work inside the plant, and the workers must take a shower before resuming their own clothes. The working garments are laundered within the plant itself. Where there is considered to be any unusual risk for which the normal precautions might not be adequate, air-fed pressurized suits are worn (figure 3).

All air extracted from the plant is filtered before release to the external atmosphere—through a 150 ft stack—by a bank of 'absolute' filters. Within the plant, control is maintained by continuously monitoring the atmospheric-beryllium levels. This is done in a variety of ways, consisting essentially of sucking a known volume of air through a filter paper and analysing the entrapped material by means of a refined spectrographic technique capable of detecting as little as 5×10^{-8} g of beryllium. With such rigorously controlled working conditions, atmospheric contamination can be kept below specified tolerance levels and the metal processed without risk.

BERYLLIUM RESEARCH

The main aims of beryllium research are to give the metal more uniform room-temperature ductility and to improve its workability at higher temperatures by eliminating minima in the ductility/temperature curve.

In order to make beryllium satisfactorily ductile at room temperature the principal difficulty to be overcome is that of cleavage fracture on the basal plane. Reasons for the observed behaviour may be of two basic kinds, one deriving from the fundamental properties of metallic beryllium itself and one due to impurities. If the fault lies with the metal, it must be assumed that the interatomic bonding within the planes on which premature fracture occurs is very much stronger than that between them, that is, the crystal has a layered structure similar to that of graphite, involving partially directed bonds and implying some departure from ideal metallic behaviour. If this type of explanation is true, the only way in which the situation can be improved is to alloy the beryllium with a metal which can enter into solid solution with it and by thus changing its electronic structure modify the type of bonding existing in the metal crystal, or even the crystal structure itself. If, on the other hand, impurities are playing a major role—as they could, for instance, by raising the temperature of the ductile/brittle transition undergone by many metals at low temperatures or by forming oxide layers at the grain boundaries—the choice lies between removing the impurities altogether or eliminating them from the metal crystal by a precipitation process, such as can be achieved by taking advantage of a change of solubility with temperature, or alternatively by adding an alloying element which will combine preferentially with the impurity.

Although room-temperature brittleness in beryllium could be an inherent property of the metal, it is difficult to envisage any fundamental characteristic of the beryllium crystal which could give rise to the complex ductility/temperature relationship observed, and there is growing confidence that this is an impurity effect. Again the choice of remedy lies between purification and precipitation of the impurities by heat-treatment or alloying.

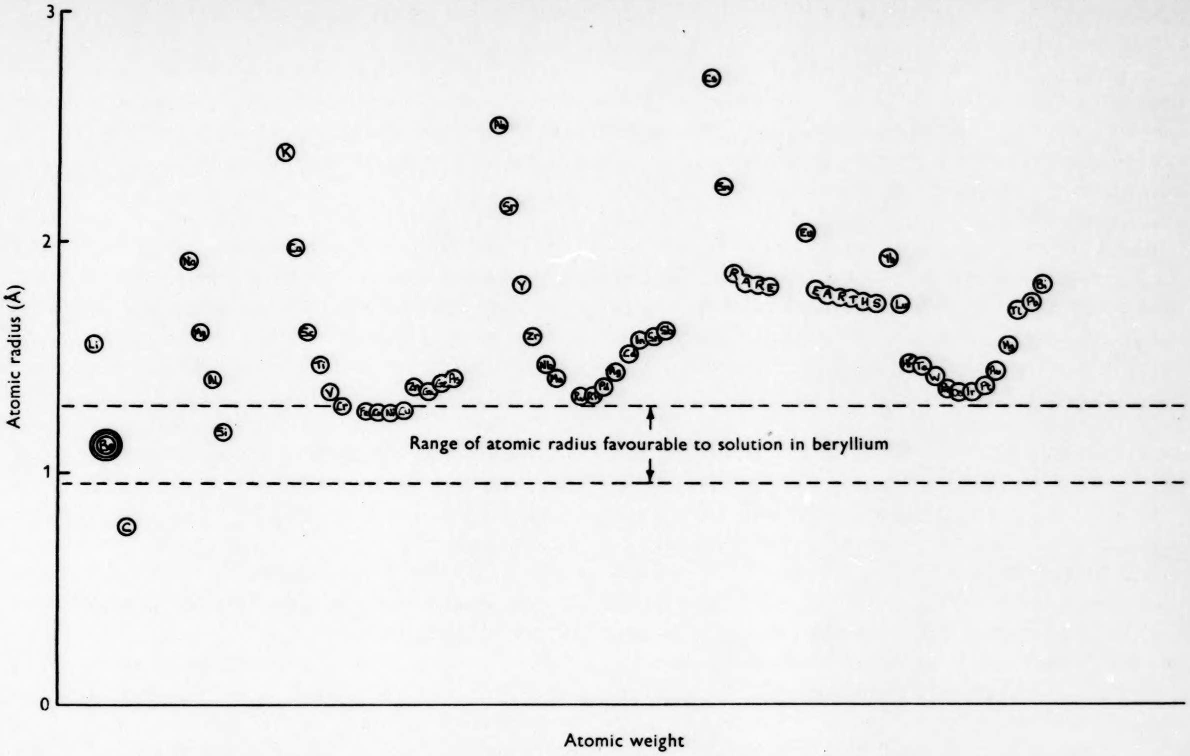

FIGURE 4 – *Atomic radii of the metallic elements. Only silicon, iron, cobalt, nickel, and copper fall within the range favourable to solution in beryllium.*

Consideration of the atomic properties of beryllium suggests that attempts to modify the electronic nature of the metal are unlikely to be rewarding. The beryllium atom is very small, having an atomic radius of 1·125 Å. Normally it is observed that extensive solid-solubility between one metal and another occurs only when the atomic radius of the solute element differs from that of the solvent element by not more than 15 per cent of the atomic radius of the latter. Consequently little solubility in beryllium can be expected from the majority of elements, since all but a few have atomic radii well outside the favourable range (figure 4). The tendency will rather be to form intermetallic compounds, more particularly as beryllium is one of the more strongly electropositive metals—a fact which favours compound formation with electronegative elements. The chance of dissolving a proportion of a substitutional alloying element in beryllium sufficient to modify appreciably the electronic characteristics of the metal seems thus to be very small. In fact only copper, palladium, nickel, cobalt, and silver have any appreciable solubility in beryllium, and even for these elements the range of solid solution is too limited to offer much hope of influencing the fundamental nature of the metal. Attempts have been made to stabilize, at lower temperatures, the body-centred cubic structure that beryllium is reported to adopt at temperatures near its melting point, by adding the more promising alloying elements, and though it might have been expected that without more extensive solid-solubility than has yet been found there would be little likelihood of success, recent work indicates that it may in fact be possible to retain the high-temperature structure at temperatures approaching the range suitable for hot working. Some consideration is also being given to the possibility of stabilizing this structure by the application of high pressures.

Any aspects of the behaviour of beryllium which are due to impurities have a considerably greater chance of being modified. Methods of purification under investigation include distillation, iodide refining, zone refining, electrolysis, and electron-beam melting. These have not yet produced a form of beryllium which is free of processing difficulties, and it is probable that the embrittling mechanisms operating involve very small quantities of impurities.

In attempting to solve the impurity problem by precipitation rather than purification, the fact that the solid solubility of most elements in beryllium is very limited helps rather than hinders, as small additions of alloying elements having a high affinity for the common impurities can be added without appreciable modification of the beryllium itself. A full exploration of the possibilities of precipitation by alloying additions and by heat-treatment forms an important part of present-day beryllium research. Hydrogen, oxygen, nitrogen, iron, aluminium, and silicon have all at some time been suggested as the impurity responsible, and current work may be expected to define the part played by these elements more accurately.

Some of the research effort available for beryllium is being devoted to a study of dislocation movements in beryllium crystals, which should clarify the reasons of the room-temperature brittleness of the metal and establish the mechanisms by means of which impurity elements can influence its deformation behaviour. The knowledge that, given a satisfactory grain-structure, beryllium can exhibit good ductility has also encouraged efforts to bring about the desired structure in material as cast.

THE FUTURE OF BERYLLIUM

Though it has required the stimulus of atomic energy to produce the effort necessary for the full industrial development of beryllium, the metal might well find other applications. The most obvious possibility is in the aircraft industry, which could take advantage of its extreme lightness and rigidity. The same qualities may also find some applications in missiles. Less dramatic uses are found in gyroscopic components, which require very high rigidity plus dimensional stability, and also in X-ray sets, for which beryllium, being transparent to X-rays, is an ideal window-material. This last application was the first industrial use of metallic beryllium.

As with so many other of the less common metals, the future of beryllium depends on its availability, its cost, and the extent to which its fundamental disadvantages can be overcome. With its unique combination of desirable characteristics, there is little doubt that a ductile and workable form of beryllium would find important applications, even if it remained very costly; but it remains to be seen whether ductile beryllium will ever be offered as an engineering material.

Although it might be argued that, if a very high degree of purification is necessary in order to obtain satisfactory room-temperature ductility and the required high-temperature properties, the full exploitation of beryllium by engineers is unlikely, it must be remembered that in the case of hafnium the dependence of its ductility on such an expensive refining process has not prevented its use. It is true that when the costly iodide-refined titanium and zirconium were the only available ductile forms of these metals no engineering applications were found for them, but the engineering developments which created the need for their specific properties did not take place until after a cheaper commercial process for the manufacture of the ductile materials had been discovered.

The nature of its processing inevitably makes beryllium expensive, but increased production can be expected substantially to reduce price. Ten years ago the American price for beryllium billet was over $100 per lb, but a demand for about 50 tons a year quickly reduced this to $47 per lb. Comment on the trends of British prices would as yet be premature, but they are not expected to exceed current American prices. In making comparisons of cost it must be remembered that beryllium is appreciably lighter than other metals, and that the figure used for most comparative purposes should be the cost per unit volume; on this basis beryllium appears in a much more favourable light. Moreover, full-scale industrial exploitation would bring about even greater price reductions than have so far occurred.

What is now needed is a better understanding of the behaviour of the metal itself and of its toxicity so that processing can be simplified and cheapened. With advances in metallurgical and medical knowledge it can be hoped that within the next few years it will become possible to assess the future of beryllium far more accurately than can be done today.

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The transport of organic substances in plants

A. L. KURSANOV

Although it has long been established that the phloem and the xylem are the media by which organic substances are transported in plants, the nature of the mechanisms involved is still obscure. In this article the author gives a general review of present knowledge and its theoretical interpretation, with special reference to recent research in the Soviet Union. He concludes with an interesting discussion of the exchange of products between mature leaves.

The old theory that substances are transported inside plants in the cells of the xylem and phloem remains unquestioned today, but many debatable problems arise when the nature of the movements, and especially that of the descending flow, is considered. During the past decade many valuable facts have been established by tracer techniques, but two conflicting theories still remain in the field. According to the first, proposed by E. Münch in 1932 [1], a solution flowing in the sieve cells carries the assimilates passively downwards, the motive force arising from the difference of turgor pressure between the two ends of the system. According to the second theory, there is no mass flow of solution, but an activated movement of molecules. The energy required is supposed to result from the metabolism of the sieve cells or their companion cells.

Neither theory has, as yet, decisive evidence in its favour. The best support for the first theory comes, in my opinion, from the work of T. E. Mittler [2] and of K. Mothes and L. Engelbrecht [3]. They have shown that after a sieve cell is punctured by an aphid it continues to exude a sucrose solution for a long period, until the exudate exceeds by many thousands of times the volume and sucrose content of a single sieve cell. This may be a pathological disturbance of the normal system, but it does suggest that a free flow of sugar solution is possible through the sequence of sieve cells.

The mass-flow hypothesis encounters a number of difficulties. Cytological observations do not normally reveal connecting channels (plasmodesmata) along which a continuous flow of solution could take place from one sieve cell to another. Moreover, if such channels exist, they must be so narrow that the resistance to flow would be far greater than can be reconciled with the rates indicated by isotopic studies. Another difficulty is that materials can move simultaneously at different rates [4, 5, 6] and even in opposite directions [7].

For these reasons we may turn to the activated-transport hypothesis, but it is still not clear how the energy of metabolism is utilized. More detailed study of the metabolism of the phloem tissue is needed, and my colleagues and I have been working in this field for a number of years. Studies carried out by M. N. Zaprometov in 1949 [8, 9] showed that amino acids moved from a solution through the cut ends of wheat stems into the ears in 50 to 100 times greater quantities than could be accounted for by carriage in the transpiration stream. This observation suggested that the transport of organic materials might be dependent on metabolism.

M. V. Turkina [10], using ^{14}C, showed in 1954 that the principal substance transported in the conducting strands of sugar beet is sucrose; a similar result had already been recorded by L. P. Vernon and S. Aronoff [11] for soya (*Glycine soja*). The results further indicated that the root of the sugar beet cannot itself synthesize sucrose [12, 13], but receives it ready-made from the leaves.

The predominance of sucrose as a transport substance has since been shown for many other species. It is especially evident in experiments carried out by M. K. Chailakhyan and myself [14] with reciprocal grafts of sunflower (*Helianthus annuus*) and Jerusalem artichoke (*Helianthus tuberosus*) arranged as in figure 1. The artichoke forms large quantities of fructosans, from the simplest to high-polymer types, while the sunflower is typified by the formation of starch and monosaccharides. When a leaf of the top component of the graft was fed with $^{14}CO_2$, it became evident that the carbohydrates synthesized travelled to the roots as sucrose irrespective of whether they were first formed in leaves of artichoke or sunflower, and irrespective of which component of the mixed plant was being traversed. The high proportion of the ^{14}C found in sucrose when the last of the different sections was analysed is also indicated in figure 1. The role of sucrose as a transport material is also well illustrated in the experiments of J. Edelman, S. I. Shibko, and A. J. Keys [15]. When ^{14}C-labelled glucose is absorbed by the scutellum of wheat or barley, it is first rapidly converted to sucrose and only then is it conveyed to the shoots and roots. In a few species sucrose appears to be replaced by analogous galactosides and in part by raffinose [16, 17]. This does not contradict the central role of sucrose and even perhaps extends it, for it shows that galactose residues can be transported when attached to sucrose.

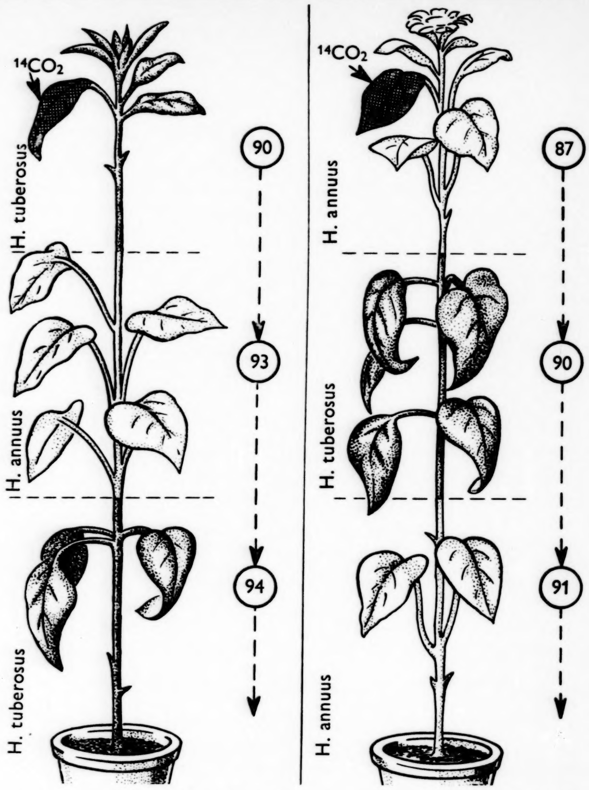

FIGURE 1 – *Grafts of sunflower and artichoke fed with $^{14}CO_2$ through the heavily shaded leaf only. The figures in circles show the percentages of the total ^{14}C in each zone recovered as sucrose.*

Amino acids, organic acids, and probably many other substances move in the phloem in addition to sugars. A detailed study has been made of the organic and amino acids in the descending current. For example, M. I. Brovchenko [5] has shown in our laboratory that, when a rhubarb (*Rheum* sp.) leaf is partly covered with a chamber containing $^{14}CO_2$, not only labelled sugars but labelled organic and amino acids can be detected in the adjacent veins within 3–4 minutes (figure 2). The amino acids generally proved to be more mobile than the organic acids, but the most significant point is that the assimilates entered the conducting tissues in proportions different from those in the photosynthesizing cells. In rhubarb the most mobile acids were malate and citrate, and among the amino acids threonine, serine, and alanine. Others, for example succinic and fumaric acids, either did not enter the conducting strands at all or did so only very slowly (figure 3). The composition of the descending solution may vary with the stage of growth of the plant. In the early autumn, the rate of movement of proline and aspartic acid diminishes, whereas that of threonine and serine remains the same and that of γ-aminobutyric acid even increases. Soya plants showed

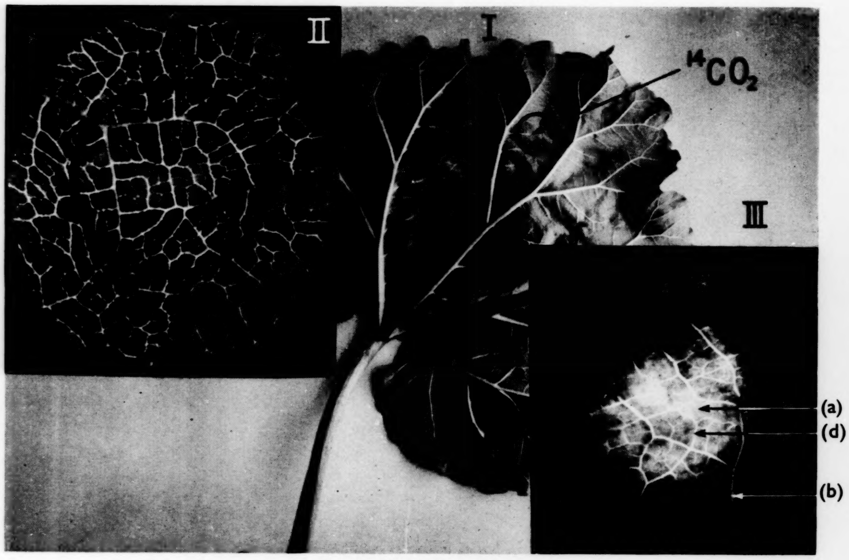

FIGURE 2 – *Underside of rhubarb leaf. In I, the dark circle shows the area to which $^{14}CO_2$ was fed; II is a portion of the same enlarged, showing the smaller veins. III is a radio-autograph showing, after a few minutes, the distribution of ^{14}C in the mesophyll* (a), *veins* (d), *and veins outside the area of supply* (b).

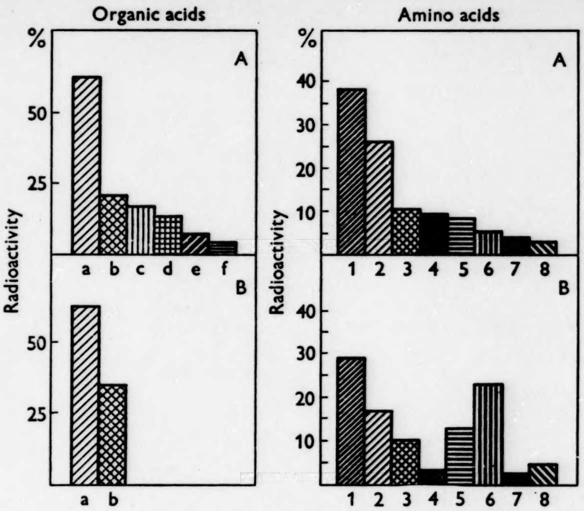

FIGURE 3 – *Distribution of* ^{14}C *in rhubarb leaf after feeding* $^{14}CO_2$ *to a restricted area. A,* ^{14}C *recovered from mesophyll; B,* ^{14}C *recovered from veins (conducting strands). The following organic acids were examined:* (a) *malic,* (b) *citric,* (c) *succinic,* (d) *fumaric,* (e) *tartaric, and* (f) *oxalic. The amino acids* (1) *serine,* (2) *alanine,* (3) *glycine,* (4) *aspartic,* (5) *glutamic,* (6) *threonine,* (7) *γ-aminobutyric, and* (8) *proline were also tested.*

similar results (C. D. Nelson and P. R. Gorham [6]). A drop of solution containing radioactive amino acids was placed on a leaf stalk from which the blade had been cut away. The different amino acids were conveyed within the plant at different rates and even in different directions. In 17-day-old plants, serine, which accumulates rapidly in young tissues, was particularly mobile, whereas asparagine and glutamine hardly moved. In older plants these relations were reversed.

The rate of movement of ^{14}C-labelled photosynthetic products has proved to be unexpectedly fast. According to the findings of M. V. Turkina and I. Dubinina [18] and N. A. Pristupa [19], it varies in grasses from 40 to 120 cm/hr and similar values have been obtained by other investigators. These rates are much in excess of any value that could be expected from simple diffusion.

Nelson and Gorham have observed still faster rates for amino acids, which are conveyed through 20- to 24-day-old soya plants at 370–1370 cm/hr and sometimes even at 3000 cm/hr. Their technique is, however, subject to the danger that some of the droplet applied to the cut end of the leaf stalk may be sucked into the opened xylem vessels. Later experiments by C. D. Nelson, H. J. Perkins, and P. R. Gorham [20], in which soya leaves were fed with $^{14}CO_2$ showed that a small part of the assimilates containing ^{14}C moved towards the roots at over 5000 cm/hr and that this was followed by the main mass of assimilates at about 100 cm/hr. It may be concluded that there are two separate mechanisms for the transport of organic materials in the phloem. Even the observation of such speeds as 100 cm/hr creates difficulties for the theory of mass flow, owing to the extreme fineness of the channels connecting phloem cells and the large differences of osmotic pressure that would therefore be required. Even for the metabolic theory they are a serious test, since they would require considerable expenditure of energy in the conducting tissue.

Turkina [21] has made an important contribution from this point of view by showing that the conducting tissues of sugar beet, *Plantago* sp., and *Caragana arborescens* have high respiratory intensities. These and similar results are summarized in Table 1. H. Ziegler [24] was able to divide the bundles of *Heracleum* into xylem and phloem; he showed that respiration was fast in both tissues.

It has been shown by Turkina and Dubinina [25] that the respiratory quotient (CO_2/O_2) of

TABLE I

Respiration rates in fibrovascular bundles and other tissues

Plants	Respiration (µl O_2 per gram of fresh tissue)			Authors
	Fibro-vascular bundles	Leaves	Petioles (without bundles)	
Sugar beet	572	416	100	Kursanov and Turkina, 1952
Sugar beet	462	232	95	Tsao-Tsung-Hsun and Liu Chin Yu, [22]
Plantago major	820	374·8	228	Kursanov and Turkina, 1952
Plantago major	500	—	146	Willenbrink, [23]
Primula beesiana	309	—	52	Willenbrink, [23]
Heracleum mantegazzianum	230	—	32	Ziegler, 1958

fibrovascular bundles is close to unity, that is, that their respiration proceeds mainly at the expense of carbohydrates. In the conducting tissues, cytochrome oxidase predominates over other oxidases, an indication of the nature of the terminal stages of their respiration.

The analyses of the phloem juice of *Robinia pseudacacia* carried out by H. Wanner [26] are frequently cited as evidence for the inactivity of sieve-tube cells, which are known to be without a nucleus after a certain age. It would, however, hardly be correct to identify the enzymatic activities of a phloem exudate from damaged bark with the enzyme complement of the protoplasm itself. Furthermore, the sieve tubes are in close connection with their companion cells and appear to form a single metabolic system.

We now have detailed knowledge of the enzymes of the vascular bundles in sugar beet (Table II). This shows that the bundles are able to activate hexoses via the hexokinase reaction. The presence of active aldolase and succinic dehydrogenase indicates that respiration is likely to proceed by way of glycolysis and the Krebs cycle. Invertase, on the other hand, is almost absent and this accounts for the relative stability of sucrose in the conducting strands.

Nevertheless, some of the sugar moving in the phloem is transformed. O. A. Pavlinova [27] showed that ^{14}C-labelled fructose moving along the conducting strands of sugar beet is converted rather rapidly into sucrose labelled equally in the fructose and glucose moieties. No labelled glucose was detectable, indicating a rapid isomerization of hexoses and utilization of their phosphoric esters for sucrose synthesis. This conclusion was confirmed by the presence of uridine monophosphate and uridine diphosphate in fair quantities in the vascular bundles. Turkina [28], using isolated bundles, showed that labelled sucrose utilized in respiration is converted within the conducting tissues to a mixture of acids including pyruvic, hydroxypyruvic, α-ketoglutaric, oxalacetic, and glyoxylic acids. These keto acids lead, by amination and transamination, to a series of amino acids that were also identified.

TABLE II

Enzymes of glycolysis and oxidation in conducting tissues (sugar beet)

Enzymes	Activity	Authors
Aldolase	+ + +	Pavlinova
Apyrase	+ +	Pavlinova
Cytochrome oxydase ..	+ + + +	Turkina and Dubinina
Phosphatase (acid) ..	+ +	Turkina and Dubinina
Phosphorylase	+	Turkina and Dubinina
α-Galactosidase	+	Pavlinova
Hexokinase	+ + +	Pavlinova
Phosphohexose isomerase ..	+	Pavlinova
Invertase	+	Turkina and Dubinina
Succinic dehydrogenase ..	+ +	Ziegler

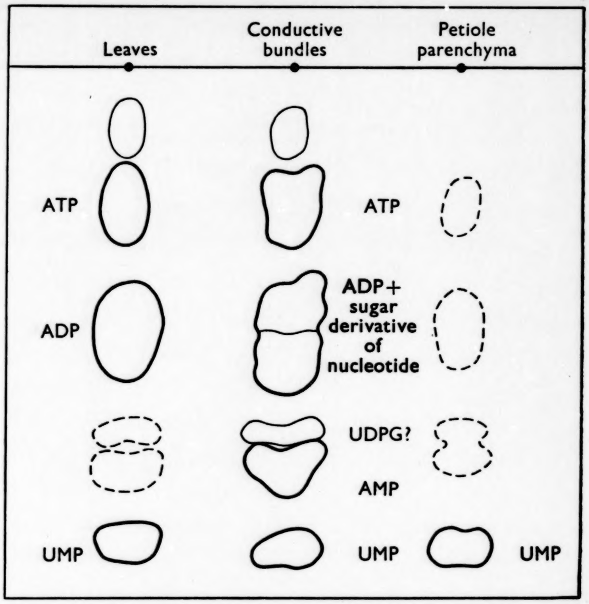

FIGURE 4 – *The acid-soluble nucleotides in the conducting tissues of sugar beet: AMP adenosine monophosphate, ADP adenosine diphosphate, ATP adenosine triphosphate, UMP uridine monophosphate, UDPG uridine diphosphate glucose.*

The principal transformations of sucrose thus occur by way of glycolysis and the Krebs cycle, giving rise to many intermediate and secondary products. The consumption of sucrose in these reactions is probably slight compared with the total amount passing through the conducting strands in the same time. Nevertheless, the intense respiration of the conducting tissues permits one to conclude that enough labile phosphate bonds (ATP) are formed for the purpose. Indirect support comes from the high activity of hexokinase and the relative abundance of nucleotides and other organo-phosphorus compounds.

Figure 4 shows chromatograms of nucleotides obtained from the fibrovascular bundles of sugar beet. Analogous chromatograms are given for the leaf blades and parenchyma of the petioles of the same plants. Comparison shows that the bundles are far richer in nucleotides than the parenchyma surrounding them or than the laminae.

We can now give a fairly detailed picture of the metabolism of the conducting tissues, but the question remains as to whether the energy liberated sets the machinery of transport in motion. The answer should apparently be in the affirmative, though we do not yet know just how the energy is utilized. It has been shown that the transport of organic materials is much retarded, or even prevented altogether, when the fibrovascular bundles are poisoned by respiratory inhibitors, such as carbon monoxide, cyanide, dinitrophenol, arsenite, azide, or iodoacetate. A similar result may also come from local cooling of the conducting tissue to 2–5° C, as was shown by O. F. Curtis in 1919. All this suggests that active metabolism in the conducting tissues is a prerequisite for normal transport of organic substances through them. The same conclusion has been reached by Nelson and Gorham [6, 29] who have shown that the transport of sucrose and certain amino acids is inhibited by cyanide, or by high temperatures: whereas the movement of sucrose and arginine, for instance, ceased entirely in damaged phloem, that of monosaccharides and asparagine continued. The latter movement may be explained by solution entering the vessel cavities of the cut xylem, a possibility not excluded by the method used.

The principal transport compounds, especially sucrose, are not sucked into the vessels because the protoplasm of the surrounding cells has a higher 'affinity' for them and so retains them. New experiments supporting this view have been carried out by Turkina [30], who has shown that fibrovascular bundles isolated from leaves of sugar beet and other plants have a capacity for accumulating sucrose greatly in excess of that of other tissues. Glucose and glycine are absorbed by the conducting strands much less, and selective absorption of sucrose may be achieved by placing conducting tissues in mixed solutions (Table III). This property is possessed by both the phloem and the xylem of the conducting strands. The accumulation of sucrose is strongly inhibited by cyanide and dinitrophenol (Table IV). We still know very little about the affinity of the conducting tissues for other materials, such as some of the amino acids; but it already appears plausible that the difference of affinity is one of the reasons for the selective uptake of sucrose and certain amino acids out of the photosynthesizing cells into the channel of flow. It may also explain why fibrovascular bundles remain rich in sucrose throughout their length while the surrounding tissues contain mainly monosaccharides.

TABLE III

Comparative absorption of ^{14}C-sucrose, ^{14}C-glucose, and ^{14}C-glycine-1 by the conducting bundles of sugar beet, September 1959. (*In counts per minute per gram fresh weight*)

Substance	Specific activity of 1 ml solution	Absorption (1 hour)		Ratio *a*/*b*
		(*a*) Conducting bundles	(*b*) Petiole parenchyma	
Sucrose ..	103 330	20 610	2880	7·2
Glucose ..	109 800	7450	3980	1·8
Glycine ..	108 870	4820	2940	1·6

TABLE IV

Influence of respiratory poisons on the absorption of sucrose by the conducting bundles of sugar beet

Duration of experiment	Solution	Absorption Counts per minute per grain	Percentage inhibition
1 hour	Sucrose	25 222	64·0
	Sucrose + KCN (10^{-3} M)	9073	
2 hours	Sucrose	52 937	51·2
	Sucrose + DNP (10^{-4} M)	25 860	

The transport of organic materials over long distances is dependent not only on the metabolism of the conducting strands but on the activities of the organs at either end. Assimilates in mesophyll cells are delivered into the conducting system very rapidly and usually independently of the concentration gradient [29, 31]. Any idea that this speed is due simply to diffusion must be given up, and an explanation sought in terms of glandular secretion or of a selective accumulation at the expense of the metabolic energy of the conducting tissues themselves. The work of Turkina just mentioned makes an active role of the conducting tissues themselves seem highly probable, but does not exclude the other possibility.

The mechanism of entry of the products of photosynthesis into the conducting system has not

TABLE V

Influence of ATP on the flow of assimilates (^{14}C) from the mesophyll into the conducting bundles in sugar beet (Counts per minute per gram)

	June		September	
	H_2O	ATP	H_2O	ATP
Mesophyll	224 490	200 040	94 760	112 540
Conducting bundles (cm)				
3–4	2470	3110	300	3450
5–6	1300	2170	230	1160
7–8	720	1130	110	740
9–10	350	870	80	280
11–12	340	530	—	—
13–14	180	320	—	—
Total entering the bundles	5360	8130	720	5630

been sufficiently studied, but it would seem that active metabolism is an essential condition. From analogy with the absorption of nutrients through the walls of the intestine, the passage of sugars from photosynthesizing cells into the conducting tissues is often thought to depend on phosphorylation. As yet there is little direct proof of this. I should like to call attention to several experiments recently carried out in our laboratory by Brovchenko. He found that enriching sugar beet leaves with adenosine triphosphate (ATP) caused a perceptible acceleration in the release of assimilates formed after feeding $^{14}CO_2$ for five minutes into the conducting strands, and a faster movement towards the root (Table v). The observations were made in the dark during a period of 25 minutes, that is, under conditions which precluded the photosynthetic formation of ATP. We are at present studying the composition of the assimilates entering the conducting system in the presence of the added ATP.

The movements of organic substances through the plant are apparently very complicated; both composition and direction of flow vary considerably for a variety of reasons. In 1953, N. A. Pristupa obtained radio-autographs from 22-day-old pumpkin plants which showed that the bulk of ^{14}C-labelled leaf assimilates moved to the root. In later experiments [19], 50 per cent was found to have reached the roots and part returned to the aboveground organs in the transpiration stream after changing their form. Thus arose the idea of a cycle of organic matter in plants.

The preferential movement of assimilates to the roots has been corroborated by many other investigators, working with annual plants up to the time of their flowering; as a plant ages the distribution of assimilates changes. This has been vividly demonstrated by I. F. Belikov [32] with soya plants in the neighbourhood of Vladivostok. Using $^{14}CO_2$ he found that the leaves of mature plants supply specific organs, or zones, with their assimilates. Low-level leaves send their products mainly to the roots but, as the fruit develops, ever increasing numbers of leaves pass their assimilates to it, and at length even those at the lower levels follow suit, and cease almost entirely to feed the roots. At this stage the plant does not react to additional

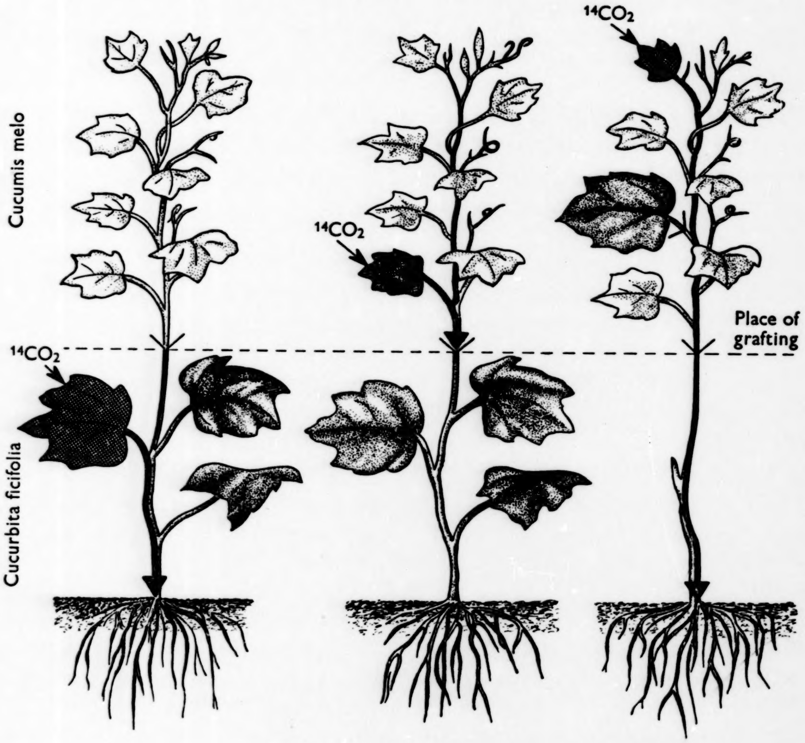

FIGURE 5 – *Graft of* Cucumis melo *on* Cucurbita ficifolia.

fertilizer, since its roots cannot form enough ion-acceptors.

Young leaves that have not completed their growth are able to photosynthesize, but do not yield their assimilates to other parts of the plant. On the contrary, they continue for a long time to receive products of photosynthesis from the nearest mature leaves. Exchange of products between mature leaves at different levels virtually ceases and it is not possible to bring about a flow of assimilates to a mature leaf even by prolonged darkening. This severe rule—the absence of mutual aid between mature leaves—may be of considerable biological importance, since it relieves the plant of the necessity of supporting leaves that are in a position unfavourable for photosynthesis.

Recent studies with tobacco plants [33] also show that ^{14}C-labelled assimilates from mature leaves continue to enter young ones for a considerable period. At the end of its growing period, a leaf absorbs and 'exports' assimilates simultaneously; in its mature state, export becomes predominant. At this stage, the flow of assimilates to the young leaves possibly goes up the xylem, into which a part of the assimilates penetrate from the phloem. This may explain why labelled assimilates could be found only in leaves above the one fed with $^{14}CO_2$ and were not found at all in the lower leaves, even though the bulk of the photosynthetic products moved down to the roots.

The distribution of assimilates in plants is probably far more complex than is suggested by these experiments. H. C. M. De Stigter [34] has shown that it is possible to graft musk-melon (*Cucumis melo*) on to *Cucurbita ficifolia* only if a few leaves are left on the stock, since the leaves of the scion do not feed the alien roots. It is enough to graft a single leaf of the stock species on to the top of the scion to start all the leaves of the scion sending assimilates down to the stock (figure 5). The nature of this effect is obscure.

It seems that the movement of organic substances in plants is multifariously regulated by means of the metabolism of all parts of the plant, and I think that the conducting cells of the phloem are no exception. We believe that more attention should be paid to the problem of the relation of metabolism to the transport of organic materials, and it is this aspect of the matter that we are trying to develop in our laboratory.

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Polarography

G. C. BARKER and G. W. C. MILNER

Diffusion near any stationary electrode is an ill-defined process and it is impossible to obtain reliable information about the composition of the solution from a study of the variations in current resulting from alterations in the potential of the electrode. This and other difficulties are avoided by using a dropping-mercury electrode, and polarography, the analytical method made possible by its use, is extremely rapid, and is applicable to very low concentrations of reducible or oxidizable substances.

When a potential difference exists between two stationary metal electrodes immersed in a solution containing oxidizable or reducible substances, reactions normally occur at the electrodes in which the cathode gives electrons to ions or molecules in the solution and the anode accepts electrons: a current flows through the cell. The size of this current depends on the composition of the solution and on the applied voltage, and some information about the composition of the solution can be obtained from a study of the relation between voltage and current. This information is only qualitative in the case of a simple cell. The current/voltage curves are not reproducible, because of the effects of the accumulation of the products of electrolysis on or near the electrodes, and because the cell current may be affected by convection currents within the solution. These difficulties are evaded in polarography—a technique originally described by J. Heyrovsky in 1922—by the use of a dropping-mercury electrode and of a 'supporting' electrolyte (see later): the current then varies in a stepwise fasion as the potential difference between the electrodes is increased; a solution containing several oxidizable and reducible substances will give a current/voltage curve from which it is possible to identify the various species and to determine their concentrations.

TECHNIQUE

The dropping-mercury electrode usually consists of a length of glass capillary tube ($\sim$0·05 mm diameter) that is attached to a reservoir of mercury by means of flexible tubing. The drops of mercury issue regularly from the tip, and fall at the rate of one every 3–6 seconds. This electrode is normally made the cathode of the polarographic cell; the anode is usually a large pool of mercury (figure 1). The dropping-mercury electrode has the advantage that contamination of the electrode surface by reaction products is avoided, as the surface is continuously renewed. It also enables polarography to be used with acid solutions, as the reduction of hydrogen ions takes place only with difficulty at a mercury surface.

To illustrate the principle of the method, suppose the electrodes to be immersed in a solution containing a few milligrams of cadmium chloride per litre. The cadmium ions near to the cathode are reduced to the metal when the cathode's potential is about 1·0 V lower than that of the anode. The cadmium metal dissolves in the mercury, forming an amalgam that is removed when the mercury drop falls. The cadmium ions, on reduction at the cathode, give up their charge; current flows between the two electrodes; and an equivalent amount of mercurous chloride is formed at the mercury-pool anode. The removal of cadmium ions from the solution near the mercury drop results in the formation of a radial concentration-gradient in that region, and cadmium ions thus tend to diffuse towards the cathode. The radial flux of cadmium ions at the surface of the mercury drop at any time is dependent on the concentration gradient, but in the case of a dilute solution it may also be affected by electro-migration caused by potential gradients within the solution. Such electro-migration is undesirable in polarography, and it is suppressed by adding to the solution a relatively large amount of an indifferent salt, known as the supporting electrolyte. The current then observed at the cathode is due only to the process of diffusion.

When the fixed voltage is replaced by a slowly increasing negative voltage, no current flows through the cell at values of the voltage below that for the reduction of the cadmium ions. After attainment of this voltage, however, reduction begins, and the concentration of cadmium ions in the solution at the electrode surface rapidly falls to a negligibly small value. As the current is simply related to the rate of arrival of cadmium

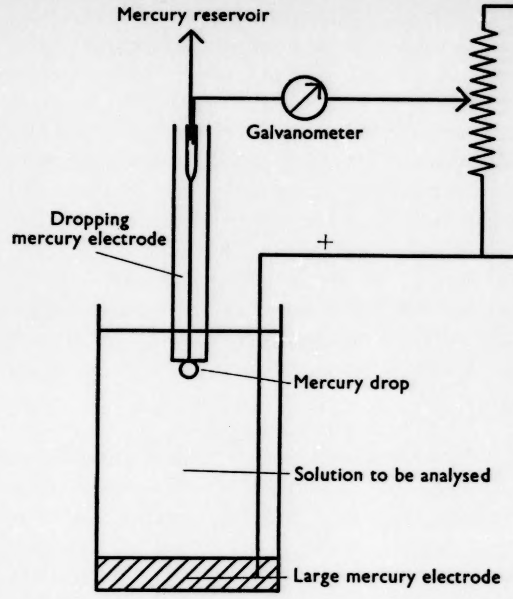

FIGURE 1 – *Polarographic cell (schematic).*

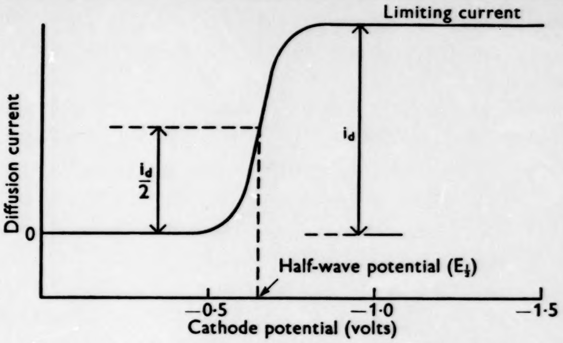

FIGURE 2 – *Idealized polarogram for a solution of a cadmium salt.*

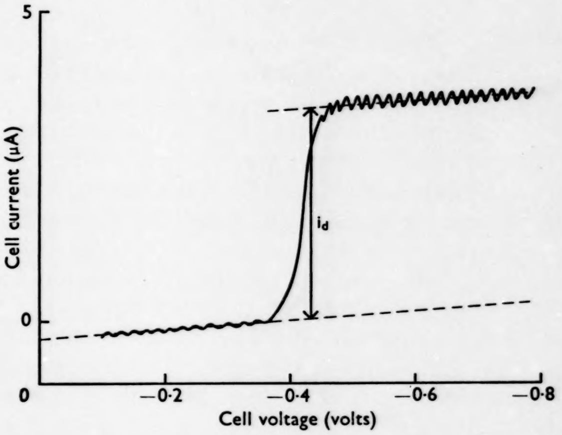

FIGURE 3 – *Typical polarogram for lead ion in potassium chloride solution.*

ions at the electrode surface, and this in turn is proportional to the concentration gradient, the current rises rapidly to a value that is not noticeably affected by further increases in the applied voltage (figure 2). This limiting value of the current (i_d) is generally referred to as the limiting diffusion-current and, provided the reduction process is diffusion-controlled, this current is proportional to the concentration of the reducible species in the bulk of the solution; this fact is the basis of the application of polarography to quantitative analysis. The limiting current varies somewhat during the life of a single mercury drop, because the drop is growing, and normally one measures its average value. This is influenced by such factors as the diffusion coefficient of the reducible species, the rate of flow of mercury, and the 'drop time'; the dependence of the current on all these factors is well understood [1, 2]. These factors are usually held constant in practical polarography, and concentrations are determined by adding known amounts of the species in question to the solution and studying the effect of these additions on the limiting diffusion-current.

A current/voltage curve of an electrode reaction is called a polarographic wave (figure 2), and the potential of the dropping-mercury electrode (with respect to a suitable reference-electrode) corresponding to the point on the wave at which the diffusion current is one-half of the limiting value is known as the half-wave potential($E_{\frac{1}{2}}$). For a given supporting electrolyte, this potential is characteristic of the ion that is being reduced and is independent of the concentration of the ion. Half-wave-potential data are therefore of considerable value in qualitative polarographic analysis.

THE PRODUCTION AND INTERPRETATION OF POLAROGRAMS

The basic equipment for plotting curves relating current and voltage is simple; it consists of a variable potentiometer to apply the polarizing voltage to the electrodes, and either a galvanometer or a sensitive microammeter for measuring the current. The basic circuit is shown in figure 1. For extensive experimental work, however, equipment that is more automatic is preferable; a motor-driven potentiometer is used, and the current is recorded photographically or by a pen recorder. A typical current/voltage curve produced by such an instrument is shown in figure 3;

this is a polarogram for a solution consisting of 1 mg of a lead salt dissolved in 10 ml of 0·1N potassium chloride. It will be seen that a very small current, the residual current, flows through the cell before the reduction potential for the lead ions is reached. This current is associated with the formation of an ionic double layer at the interface between the dropping-mercury electrode and the solution. There is no way of eliminating this background current, and a correction for it is applied graphically, as indicated in figure 3. The polarogram also shows the small variations in the recorded current caused by the growth and fall of the mercury drops.

SUPPORTING ELECTROLYTE

The choice of a supporting electrolyte depends on several factors, the most important of which is the reduction potential for the cation of this electrolyte. This potential must be appreciably more negative than the half-wave potentials of the ions which are to be determined. Potassium, sodium, and ammonium salts are often used in the determination of the baser metals; tetramethyl-ammonium salts may be used for the determination of sodium and potassium. The anion of the supporting electrolyte is also important, as the polarographic method is not completely satisfactory for the study of reductions having half-wave potentials close to, or more positive than, the potential at which anodic dissolution of the mercury electrode takes place.

When two or more ions are to be determined in the same solution, the supporting electrolyte must be carefully chosen so that the $E_{\frac{1}{2}}$-values for the various waves are separated by at least 150 millivolts, otherwise the waves tend to coalesce and the heights of the individual waves cannot be accurately determined.

Frequently the diffusion current does not rise smoothly to its limiting value in the manner indicated in figures 2 and 3 and a sharp peak is observed at the beginning of the current-plateau. Such a maximum on a polarographic wave seriously interferes with the measurement of the wave height: maxima are usually suppressed by adding a small amount of a surface-active substance to the solution.

KINETIC AND CATALYTIC CURRENTS

The discussion has been limited, so far, to diffusion currents arising from simple electrochemical reductions. In some cases, however, it is possible for a purely chemical process, either preceding or following the electrochemical reaction, to affect the polarogram. Such a situation occurs in the reduction of certain aldoses and organic acids. With the aldoses, a tautomeric transformation of the ring form into an open chain precedes the electrochemical reduction, and the diffusion current is governed by the kinetics of the chemical transformation. Such transformations can be detected only by polarographic methods. Similarly, in the reduction of certain organic acids—a good example is pyruvic acid—only the undissociated form of the acid is readily reduced; again, the current is controlled by the rate of a chemical process.

Other reactions can give rise to catalytic currents. An example is the iron-catalysed hydrogen peroxide current. The reduction of ferric ions at the dropping-mercury electrode leads to the formation of ferrous ions. If hydrogen peroxide is present in the same solution, these ferrous ions are re-oxidized chemically to ferric ions while still in the neighbourhood of the dropping-mercury electrode, and they are thus again available for reduction at this electrode. The additional current caused by the presence of hydrogen peroxide is referred to as the catalytic current, and studies of this current have led to values for the velocity constant of the chemical reaction in fair agreement with values obtained by other methods. Another type of catalytic current is given by proteins when present in an ammoniacal solution. The current in these cases is due to the evolution of hydrogen, a process catalysed by the protein in solution.

APPLICATIONS OF CONVENTIONAL POLAROGRAPHY

Although there are many fields of application for the technique, its main use is in analytical chemistry. The limits of concentration for analytical determinations are from 10^{-2} to 10^{-5} M, application to lower concentrations being prevented by the occurrence of the residual current. It is possible to measure concentrations in the range 10^{-2} to 10^{-4} M with an accuracy of about ± 2 per cent; the polarographic method is very suitable for trace-element analysis, for which the accuracy and reproducibility of the results are adequate. Moreover, determinations can often be completed in a fraction of the time needed for chemical methods, as there is, in many cases, no need for any lengthy chemical pretreatment of the sample. Human factors play a smaller part in polarography than in most analytical methods, especially when polarograms are recorded by automatic means. Such polarograms can be similarly interpreted by different workers, and the results can be checked at any time, as a permanent record is obtained. The advantage of this in routine analysis is readily apparent.

METALLURGICAL AND INORGANIC ANALYSIS

The uses of polarography in metallurgical analysis are very extensive and cover the determinations of trace amounts of Cu, Pb, Sn, Cd, Ni, Zn, and other elements in a wide range of ferrous and non-ferrous materials. In many cases it is necessary only to dissolve the sample in a mineral acid, but in some instances some means of preventing interference from a readily reduced major constituent of the sample must be employed. The simpler techniques for removing such interference involve changing the valency of the interfering element or the addition of a reagent to form a stable complex with the interfering species. Complex formation moves the polarographic waves to more negative potentials, and the value of this technique is exemplified by the analysis of copper alloys for lead and nickel. These alloys can easily be dissolved in hydrochloric acid, but unfortunately the polarogram of the solution shows a large wave due to the reduction of copper ions before those for the reduction of the ions of lead and nickel, which are present in brass. However, the determination of the lead and nickel contents can be completed polarographically without any further difficulty if the sample solution is made alkaline, and cyanide added to form complexes with the copper and zinc ions.

The uses of polarography in inorganic analysis are very numerous and include the determination of various inorganic constituents in ores, minerals, rocks, waters, inorganic chemicals, organic preparations, paint pigments, propellants, dyestuffs for use in foods, and such biological materials as plants and soils. Further details of the methods used in these branches of analysis are given in treatises on polarography [1, 2].

The polarographic method is not limited to ions that undergo reduction or oxidation at the dropping-mercury electrode. Elements whose ions are neither reducible nor oxidizable include thorium, zirconium, hafnium, and tantalum, but indirect methods are available for the determination of at least two of these elements: both thorium and zirconium can be precipitated with *m*-nitrobenzoic acid, and, after filtration and re-solution of the precipitate in mineral acids, the metal can be determined indirectly from the polarographic wave of the nitro-groups in the precipitate.

ORGANIC ANALYSIS

Polarography is not as widely applicable to organic analysis as to inorganic analysis. Numerous organic substances are reducible at the dropping-mercury electrode, but many of these reductions are irreversible processes giving rise to polarographic waves that approach their maximum heights rather slowly. Such waves are not generally as readily evaluated as those encountered in inorganic polarography. Moreover, hydrogen ions participate in the reduction of many organic substances, and it is necessary therefore to use solutions in which the hydrogen-ion concentration is carefully controlled. Another important consideration is the low solubility of many organic materials in aqueous solutions: analysis must sometimes be carried out with mixtures of organic solvents and water, or with non-aqueous solutions. Alcohol-water mixtures frequently give satisfactory results, and, among the non-aqueous solvents, ethylene glycol, dioxan, pyridine, and alcohol have proved useful. Organic compounds that undergo reduction at the dropping-mercury electrode generally contain reducible groups or conjugated double bonds, and useful waves are given by aldehydes, ketones, aliphatic and aromatic nitro-compounds, azo-compounds, vitamins, steroids, sulphur compounds, and organometallic substances [1, 2].

GAS ANALYSIS

Oxygen undergoes reduction at the dropping-mercury electrode to give two waves of equal height. The first of these is suitable for the determination of oxygen in various materials, including liquids, gases, and solids. The continuous determination of the concentration of dissolved oxygen in natural waters is possible when a dropping-mercury electrode with a wide bore is used. Polarography can also be used to study the oxygen content of blood plasma, and to investigate respiration and photosynthesis in living cells, such as in green algae.

USE IN TITRATIONS

The dropping-mercury electrode may be employed to determine the end point in a chemical titration. A typical example is the titration of lead with dichromate ions. The diffusion current given by an applied potential difference of 1·0 V will fall as the dichromate solution is added, until the end point is reached; after this, it will rise

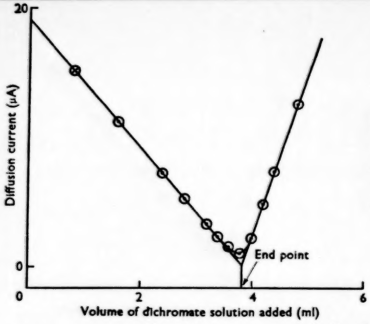

FIGURE 4 – *Titration curve of lead nitrate solution with potassium dichromate solution.*

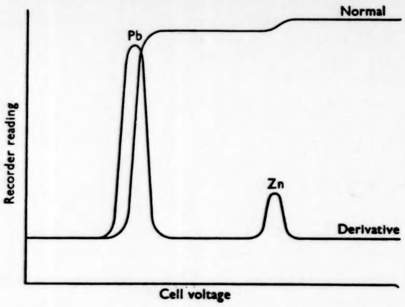

FIGURE 5 – *Normal and derivative polarograms (idealized) for a solution containing zinc and lead ions.*

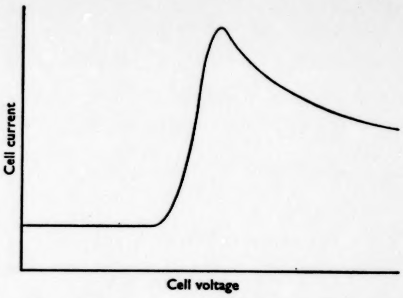

FIGURE 6 – *Current/voltage curve in oscillographic polarography.*

again. An extrapolation of lines drawn through the experimental points to their intersection gives the position of the end point (figure 4). This technique is also applicable when the species to be determined is reducible and the titrant is not reducible, and vice-versa. The break in the current/volume curve is not always sharp, because of the solubility of the precipitate, but this usually causes little difficulty in fixing the end point. This technique is used mainly for precipitation reactions, although there are some titrations based on complex ion formation.

DERIVATIVE POLAROGRAPHY

Attempts have been made, during the last ten years, to increase the resolving power of the polarograph by recording the rate of change of the current flowing in the cell as the applied voltage increases. These 'derivative polarograms' will show a maximum at the half-wave potential. The technique is particularly useful in the determination of a reducible ion in the presence of a larger concentration of a more readily reducible ion (figure 5).

Derivative polarograms may be obtained by immersing two synchronized dropping-mercury electrodes in the sample solution. The polarizing circuit for these electrodes is so arranged that the potential of one electrode lags behind that of the other by a small, constant, amount, and the current-recording circuit is modified to measure the difference in the diffusion currents at the two electrodes. Several variations on this method have been described [3, 4], but an alternative method which can be used with a normal polarographic cell has been more widely adopted because of the difficulties arising from the use of synchronized electrodes [5, 6]. Basically, this second method involves merely the insertion of some type of differentiating circuit in one of the electrical connections to the polarographic cell. The differentiating circuit may be a large condenser connected in series with the galvanometer or recorder, or it may be a relatively complex electronic circuit.

A.C. POLAROGRAPHY

Methods such as those mentioned above cannot increase the sensitivity of the conventional polarograph, and several new types of polarograph have been developed in recent years to meet a growing need for increased sensitivity combined with high resolution. These instruments produce derivative polarograms recording the alternating component of the cell current when a small alternating voltage is superimposed on the slowly changing voltage applied to the electrodes of the polarographic cell. The simplest of these instruments utilizes a small, sinusoidal, voltage, and the periodic component of the cell current then is the sum of two sinusoidal currents, one of which is connected with the ionic double-layer at the surface of the dropping-mercury electrode and the other with variations in the diffusion current produced by the small rapid changes in the cell voltage. The difference between the phases of these currents can be used to obtain a polarogram which shows principally the variation of the alternating component of the diffusion current with the average value of the cell voltage. This polarogram has much the same general shape as a derivative polarogram obtained by simpler methods, but reducible ions can be detected at an appreciably lower concentration than with the simpler instrument.

Even higher sensitivity is obtainable if a square-wave voltage is used in place of the sinusoidal voltage, as the former type of polarizing voltage permits a better separation of the periodic component of the diffusion current from the much larger current arising from the ionic double-layer. With a square-wave polarograph, reducible ions can be detected when their concentration is as small as 4×10^{-8} M, and high sensitivity is obtained even in the presence of large amounts of ions that interfere with the operation of the conventional polarograph [7]. For example, trace constituents in steels can be determined polarographically when the sample solutions contain gross amounts of readily reduced ferric ions. Many important applications for the square-wave polarograph have already been found in the analysis of such materials as alloys, natural waters, trade effluents, foodstuffs, fertilizers, and minerals [8].

The pulse polarograph is yet another of the electronic instruments developed in recent years to give both high sensitivity and high resolution [9]. This instrument applies small, rectangular-wave, voltage pulses ($\frac{1}{25}$ sec duration) to the electrodes of the polarographic cell. Each pulse occurs at a predetermined time in the life of the mercury drop, and the pulses are superimposed on a slowly changing voltage such as is employed in conventional polarography. Electronic circuits are used to measure the changes in diffusion current produced by the pulses. This instrument is appreciably more sensitive than the square-wave polarograph, especially for the determination of irreversibly reduced substances such as oxygen, hydrogen peroxide, and many organic compounds. There are many applications for this instrument in inorganic and organic analysis.

OSCILLOGRAPHIC POLAROGRAPHY

One further important development in recent years is a polarograph which displays a polarogram of a rather unusual form on the screen of a cathode-ray tube [10]. This polarograph applies to the electrodes of the cell a rapidly changing voltage that starts to change at a definite moment in the later part of the life of the mercury drop. The whole or part of the useful range of potential of the dropping-mercury electrode can thus be explored within the life of a single drop, and a polarogram is displayed almost continuously on the screen of the cathode-ray tube. When this type of instrument is used, the diffusion current produced by a simple reduction rises rapidly to a maximum value at a potential near to the normal half-wave potential and then decays slowly as the potential of the cathode becomes still more negative (figure 6).

Oscillographic polarography permits determinations to be carried out with great rapidity and with about the same accuracy as is obtained in conventional polarography. High resolution is obtained, and interference from a readily reducible major constituent can be largely avoided by making the potential of the dropping-mercury electrode before the start of the voltage sweep somewhat more negative than the half-wave potential for the reduction of the interfering ion. In favourable circumstances, reducible ions can be determined at concentrations down to about 5×10^{-7} M. This type of instrument, the single-sweep oscillographic polarograph, is used for routine analysis in many laboratories.

This instrument, and other modern instruments, make extensive use of electronic circuits to obtain improved performance and, as yet, the reliability of these instruments compares unfavourably with that of the conventional polarograph. When this defect is remedied, as it can be by using recent developments in the field of semiconductors, these instruments should play an important part in the further development of polarography as an analytical method. It also seems likely that some of them will be used to cast light on such fundamental problems as the mechanisms of electrode processes at mercury and other electrodes.

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Problems of growth and calcium deposition in reef corals

T. GOREAU

The corals are a group of animals closely related to the sea anemones; they differ from them in being able to form massive calcareous skeletons that eventually become large, dense colonies. This article describes recent work using radioactive isotopes to study the mechanism of growth and calcium deposition in these colonies, and the formation of coral reefs.

Coral reefs form the most extensive marine communities known on this planet at the present time. Some of them have been in continuous existence for over 50 million years. Because corals form massive skeletons of calcium carbonate, the long-continued deposition of this has resulted in the accumulation of reefs, some of which are several thousand feet thick. As such, the reef corals are important land builders in tropical areas, frequently forming whole new islands and strikingly altering the shorelines of continents. The study of reefs is also of special interest because limestone formation takes place here under much the same conditions as must have occurred during earlier times in the earth's history. The simple methods of descriptive natural history and field geology, such as those used in the 1830s by Charles Darwin and James Dwight Dana in their classic work on the origins of coral islands, are today supplemented by a variety of new techniques, ranging from free diving to mass spectrometry and micropalaeontology.

The biological study of corals began with the taxonomic investigations of Lamarck and Milne-Edwards, among others, in the early nineteenth century. The principal features of the anatomy, histology, and embryology of the corals were worked out by the early part of this century; such investigations continue today using the new techniques of electron microscopy and chemical cytology. Towards the end of the nineteenth century, Alexander Agassiz started his important work on the growth rates and ecology of reef corals. Similar studies were later carried out on a world-wide scale by others [1], thus establishing the significance of coral reefs in relation to major changes in land and sea-level, especially during the Pleistocene geological period. Recent work by ecologists has also brought to light the amazing ability of coral-reef communities to maintain a very high productivity and standing crop of organic matter, despite the fact that most reefs occur in the impoverished surface waters of tropical seas.

The experimental investigation of the reef-building corals as such started only about fifty years ago. The physiological studies carried out on nutrition and growth of corals by members of the British Great Barrier Reef Expedition of 1928–29 are an outstanding example. Important contributions to our knowledge of reef-coral physiology and biochemistry were also made by Japanese marine biologists working in Palau before World War II. Nevertheless, there are still major problems of fundamental importance to be solved, and it is the object of this paper to deal with some of these within the framework of our own recent studies on reef-coral skeletogenesis.

The true reef-building corals are limited in geographical distribution to the clear warm sunlit waters of tropical oceans; they centre upon the great reef-tracts of the Indo-Pacific and Western Atlantic coral seas. The unit of structure in most reefs is the coral polyp. However, the building activities of the corals are often enhanced by the calcareous algae, which cement and consolidate the coral framework into a solid mass of limestone.

The so-called stony corals, the Madreporaria or Scleractinia, are an order of animals belonging to the phylum Coelenterata, class Anthozoa, subclass Hexacorallia [2]. Their most striking feature is their ability to form a massive, calcareous skeleton, which forms a supporting base upon which the polyps live (figure 1). Although an individual polyp is only of the order of 10 mm in diameter, such skeletal masses often grow to enormous sizes as a result of colony formation by the asexual division of mature polyps. Individual coral-colonies weighing several hundred tons and large enough to fill a large living-room are common on many reefs. The closest relatives of the true corals are the non-calcareous sea anemones, familiar to anyone

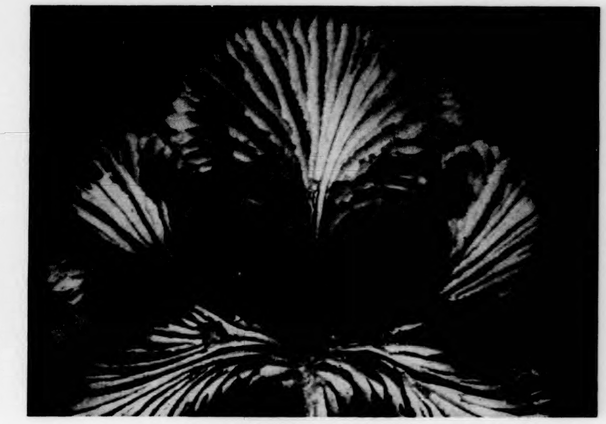

FIGURE 1 – *Skeleton of* Colpophyllia natans, *a reef-building coral. A young colony is shown; the fleshy parts have been removed. The radial lines are the calcareous ribs.*

who visits the seashore. The corals resemble the anemones in basic body structure and overall appearance; they differ in that their basal disk is gossamer-thin and highly folded, offering an enormous surface area for limestone secretion.

The terms growth and skeletogenesis, in this paper, refer to the calcification of corals. The terms polyp and corallite are used interchangeably here to describe the individual animal unit of a coral colony. The word 'coral' is itself confusing, as it is used by laymen to describe practically any branching calcareous or horny growth of marine origin. In this paper the term coral refers specifically to Madreporaria or Scleractinia, but not, for example, to seafans or the precious 'red coral' that belongs to the Octocorallia, or the 'stinging coral', which is a calcareous hydrozoan. In the corals, the calcareous skeleton is called the corallum or sclerenchyme; the fleshy parts are collectively known as the polyparium or the coenenchyme. Sharp distinctions are usually made in the technical literature between the deep-water, non-reef-building corals and the tropical, shallow-water, reef-building corals.

A remarkable feature of all reef-building corals is their symbiosis with unicellular algae known as zooxanthellae. Tropical shallow water corals contain large numbers of these within specialized carrier cells in the gastrodermal epithelium. The zooxanthellae are Dinophyceae, a group to which many of the free living marine flagellate algae also belong. An electron micrograph of zooxanthellae is shown in figure 8.

TECHNIQUES

There is one major obstacle to the study of the growth of corals. This is the difficulty of keeping corals alive and healthy in laboratory aquaria for sufficient time for accurate growth-measurements to be made. Such experiments take weeks or even months. We wished to devise a more rapid method, and we started four years ago to develop isotope-tracer techniques using radioactive calcium-45. Corals are unable to distinguish between the stable and radioactive varieties of calcium; both isotopes are deposited into the skeleton in the same ratio as they are present in the medium. The amount of radioactivity taken up under various controlled experimental conditions is therefore an index of growth and physiological function [3]. This technique is so sensitive that growth can be measured in corals that have been exposed to calcium-45 for only a few hours, and it can be adapted to the study of coral growth in the actual

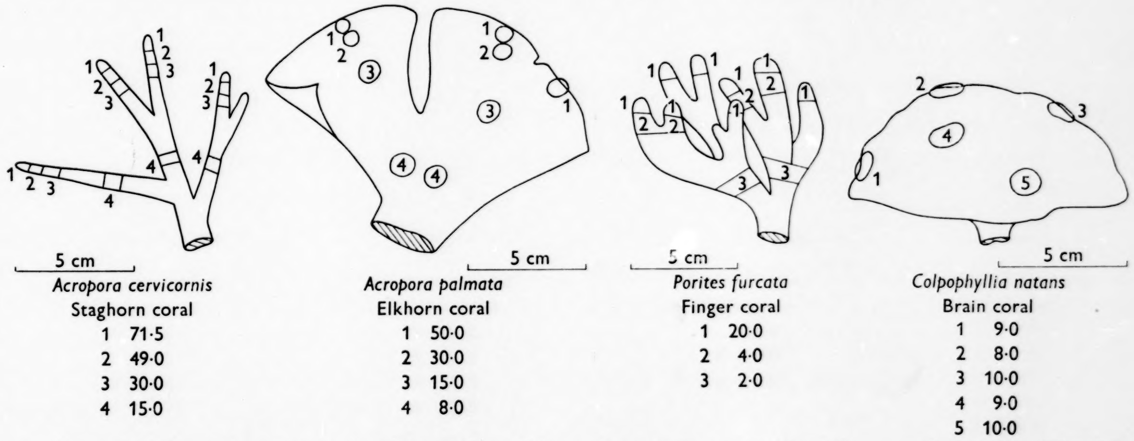

FIGURE 2 – *Axial growth gradients in three species of branching corals compared with a massive coral. The figures below each specimen are the average growth-rates, given in μg Ca per mg of tissue nitrogen per hour, in the different parts of the colonies that are identified by numbers.*

FIGURE 3 – Meandrina braziliensis, *a free-living coral. This young colony is shown in the feeding attitude, and is completely expanded, with a large number of tentacles bearing batteries of nematocysts, which can be seen as small white spots.*

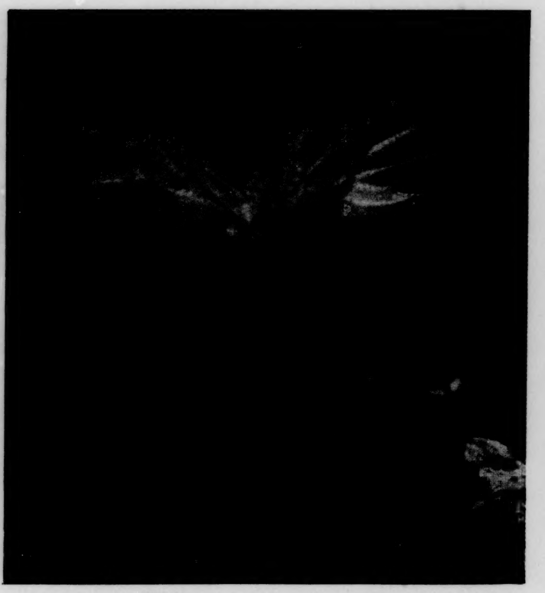

FIGURE 4 – Tubastrea tenuilamellosa, *a typical non-reef-building coral. Unlike the other species shown here, this coral has no zooxanthellae.*

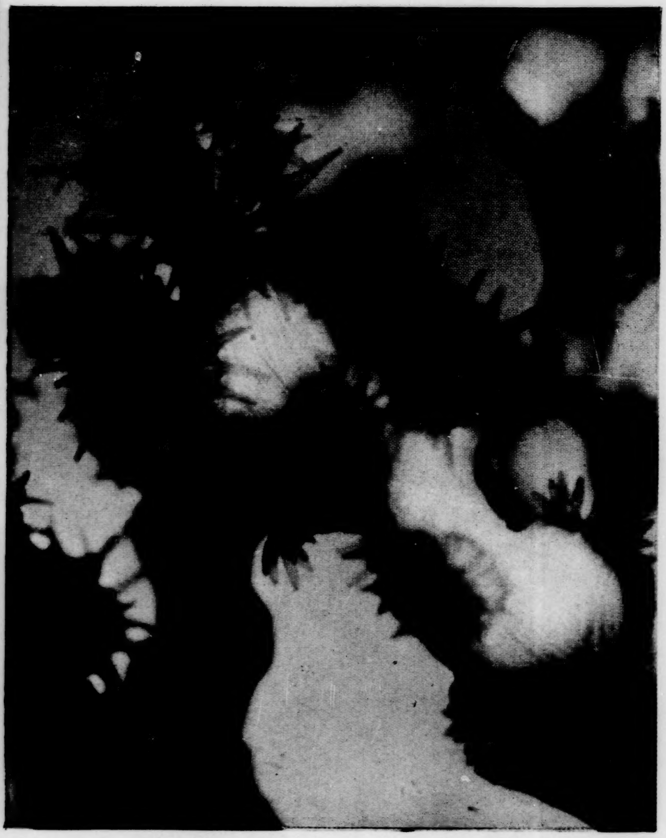

FIGURE 5 – Oculina diffusa, *a small branching coral. The colour is due to the zooxanthellae. The corallites are about 5 mm in diameter.*

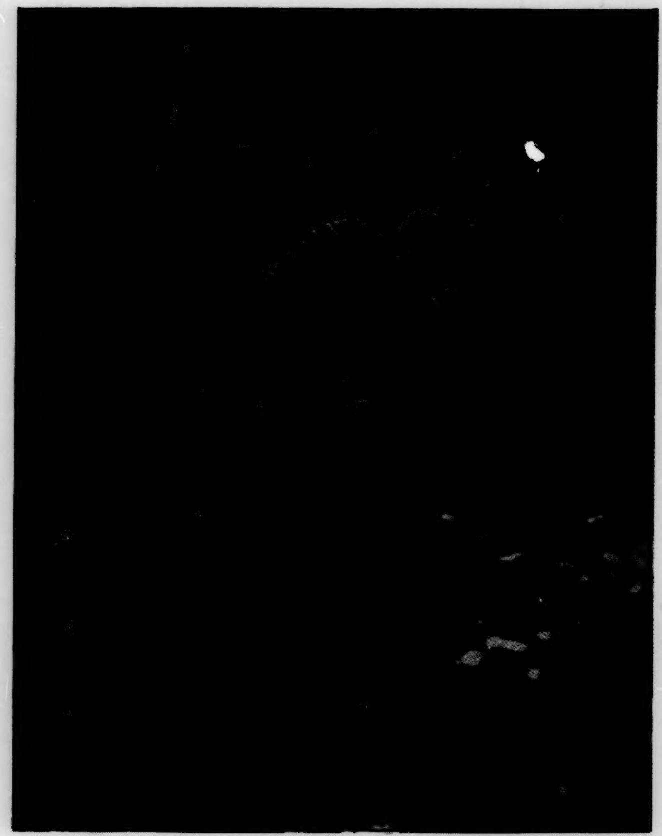

FIGURE 6 – *Underwater photograph showing the side of a coral buttress at a depth of 20 ft. The large round masses in the centre are reef-building scleractinian corals. The plate-like forms in the upper right-hand corner are colonies of* Millepora, *the poison 'coral', a reef-building hydrozoan.*

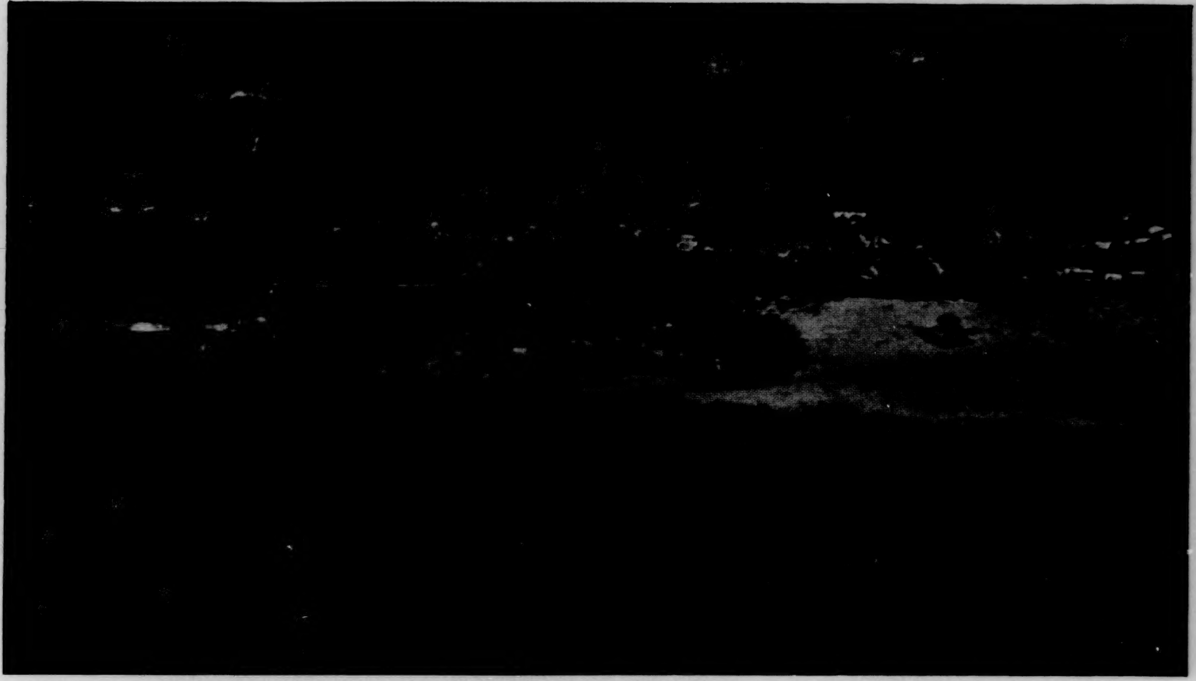

FIGURE 7 – *Aerial view of a fringing reef near Ocho Rios, Jamaica, showing marked structural zoning. The reef is separated from the shore by a light-blue shallow lagoon. The distance across the middle of the photograph is about 700 yards.*

reef [4]. As only small samples are needed for analysis, it is possible to measure differences in the growth rate in various parts of a single colony or even within a single corallite. Although many basic questions of coral skeletogenesis remain to be answered, the use of these new techniques has at least made it possible to describe some of the factors that control and influence the calcification reaction.

FACTORS REGULATING GROWTH RATE OF CORALS

The most important of the intrinsic factors influencing calcification in corals are the species; position in the colony; the age of the colony; and enzymes.

Although reef-building corals grow in fairly uniform conditions of temperature, water circulation, and illumination, we have consistently found very large differences in the growth rates of different species. The highest rates are invariably found in the branching, acroporid corals (the West Indian elkhorn and staghorn corals), with Millepora (a hydrocoral-line) a close second, and the Poritidae (finger corals) third. The various massive corals are usually slower [4].

The position in the colony affects the growth rate in the branching corals, but not in the massive corals. In the former we found that most of the growth took place in the terminal corallites at the tips of the branches; in the latter the rate was more or less the same all over [4] (figure 2). The factors that determine the polarity of growth are not understood. In the staghorn corals, new branches may arise almost anywhere on the older parts of the colony. Their appearance is heralded by the differentiation of large pale apical corallites; these are very different from the much more numerous small dark polyps that form the sides of the branches. In the finger corals, on the other hand, new branches arise mostly through the dichotomous growth of older branches, and there is little obvious differentiation of the apical polyps, save for their much greater growth-rate.

The effect of age on growth-rate is considerable in some corals, negligible in others. T. Stephenson and A. Stephenson [5] showed that the growth-rate of some corals decreased in inverse proportion to their size and age. In the West Indian rose coral (*Manicina areolata*) we found that colonies weighing approximately 0·05 g deposited calcium nearly one hundred times faster, per unit of tissue nitrogen, than did colonies weighing 150 g

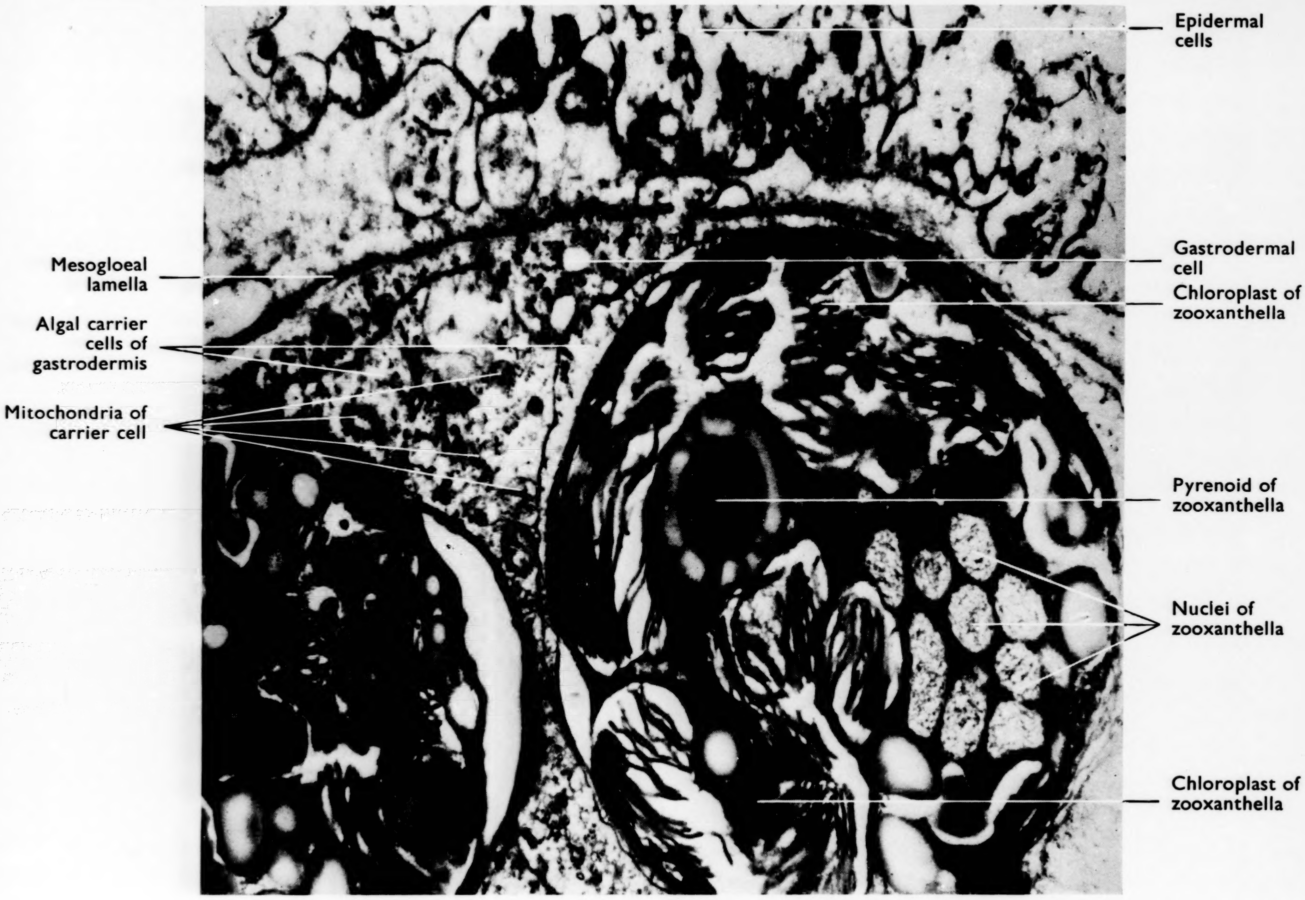
Epidermal cells
Mesogloeal lamella
Gastrodermal cell
Chloroplast of zooxanthella
Algal carrier cells of gastrodermis
Mitochondria of carrier cell
Pyrenoid of zooxanthella
Nuclei of zooxanthella
Chloroplast of zooxanthella

FIGURE 8 – *Electron micrograph of two zooxanthellae in the gastroderm of a coral. Magnified* 17 400 *times. The zooxanthellae are contained within specialized carrier-cells, which can be seen as protoplasmic rings surrounding the algal cells. Note the mitochondria in the cytoplasm. Each zooxanthella contains a nucleus, pyrenoid, and chloroplast, the last of which may be seen as the large striated horseshoe-shaped object that nearly fills the algal cell.*

[6] (figure 9). We believe that this phenomenon may be connected with the peculiar mode of life of the coral. *M. areolata* is usually found unattached, and on sandy or soft grassy bottoms where a heavy skeletal mass would result in the colony's sinking into the sediment. The slowing of the growth-rate with increasing size may thus be an adaptive mechanism for limiting the size of the species in response to the necessity of keeping 'afloat' on top of shifting, unstable, bottom-sediments. We do not believe it likely that there is much slowing down of growth with age or size in those hermatypic corals that habitually reach great sizes on the reef, or in branching species in which colony growth is indeterminate, resulting in the formation of irregular underwater coral-hedges, often many acres in extent.

We have so far investigated two enzymes to see if they are connected with calcification in the corals. The finding of alkaline phosphomonoesterases in corals [7] led us to propose that phosphatases were involved in calcification; subsequent histochemical studies showed that these enzymes were absent from any structures associated with skeletogenesis [8]. In a series of unpublished experiments we demonstrated that most coelenterates, including all twenty-four species of coral tested, contained high concentrations of carbonic anhydrase. This enzyme catalyses the reversible hydration of CO_2 to H_2CO_3 and also the dissociation of carbonic acid to carbonate. Carbonic anhydrase has been shown to be involved in carbonate shell deposition in the chicken egg [9], the oyster [10], and the barnacle [11]; we therefore investigated the possibility that it also plays a role in coral skeletogenesis. The use of low-toxicity specific carbonic-anhydrase inhibitors brought about a remarkable reduction in the calcium-deposition rate in corals. When the corals contained zooxanthellae, the reduction of the growth-rate was far less in the light than in the darkness; if zooxanthellae were absent, the degree of inhibition was the same in light as in darkness, and the growth-rate fell to extremely low levels [3]. A discussion of the significance of these findings will be deferred until later.

Light appears to be the most important of all the environmental factors that control the calcification rate of hermatypic corals in the reef. It has long been known that reef-building corals can grow well only in shallow water where the light is intense enough to allow a net excess of photosynthetic production of organic matter by plants. Reef corals always grow towards the light, and they are hardly ever found in caves or other dark places where there is too little light for photosynthesis in the zooxanthellae.

We designed experiments to test the effect of variations in light intensity upon the rate of calcification of reef-building corals under approximately natural conditions; we found that calcium uptake is fastest at noon on a clear sunny day; is reduced by approximately 50 per cent on a cloudy day; and is reduced by an average of nearly 90 per cent in total darkness [4]. The light : dark ratio in the calcification rates of different species varied between approximately 3 : 1 and 23 : 1, averaging 10 : 1. This striking dependence of coral growth-rates on ambient-light intensity is dependent on the presence of the zooxanthellae; this is shown by the extremely low calcium-deposition rates of otherwise healthy reef corals from which the zooxanthellae have been removed by culturing in total darkness for several months before the experiment. The calcification rate of such colonies was very low and was independent of the light intensity [3].

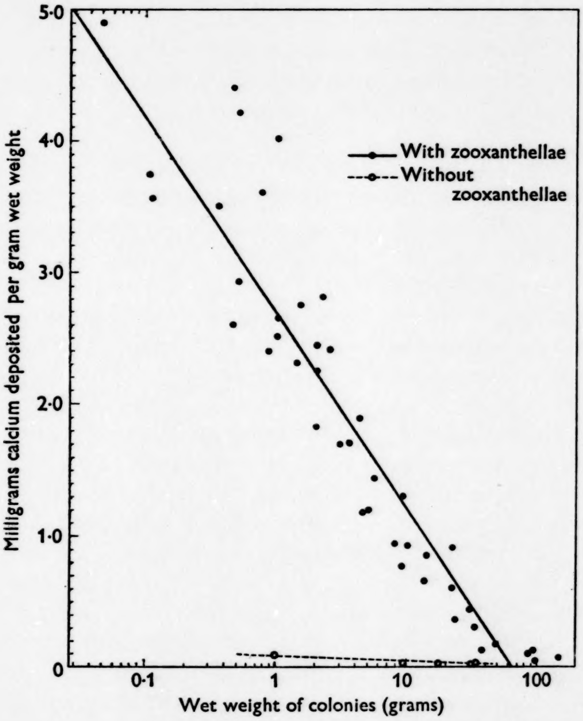

FIGURE 9 – *Calcification rate plotted against size in* Manicina areolata, *a small free-living brain coral. The data show that the smallest colonies grow approximately* 100 *times faster per unit weight of coral than the largest.*

THE COMPOSITION OF THE CORALLUM

An important, and still largely unsolved, question of coral calcification concerns the origin of the calcium deposited by the corals. Since most of our experiments were carried out on non-feeding corals exposed to radioactive calcium added to the water as $^{45}CaCl_2$, it is fairly clear that the corals must be able to absorb Ca^{++} directly from seawater, and that very little is derived from their food, which consists of small planktonic animals. Indirect support for this view is provided by evidence that corals are apparently unable to discriminate calcium from strontium, so that both elements are deposited in the skeleton in the same proportions as they exist in seawater [12]. Most organisms, especially the crustacea that form a large part of the food supply of corals, appear to exclude strontium; the coral shows no sign of this discrimination as it would be expected to do if its calcium were derived from its food.

There is no definite information about the mechanisms responsible for transport of the calcium inside the coral. Calcium does not appear to be concentrated in the tissues before deposition in the skeleton; on the contrary, corals tend to have a lower concentration of calcium in tissues than there is in seawater [13]. As $CaCO_3$ is slightly soluble in seawater, there is a considerable amount of equilibrium exchange of calcium between the corallum and the medium; no net solution can occur under normal conditions, because the seawater in coral reefs is supersaturated with respect to $CaCO_3$. The tendency of the corallum to exchange calcium with the seawater is drastically reduced as long as it is covered by a living, intact sheet of polyps. This protective action disappears as soon as the polyparium is killed; the equilibrium exchange rate then increases by several orders of magnitude. This shows that the polypary layer is fairly 'calcium proof', and that it effectively isolates the skeleton from the environment as long as it is alive [14]. This is the opposite of what is seen in vertebrates, where the calcium of the bone remains relatively mobile and freely exchangeable with the calcium dissolved in the body fluids.

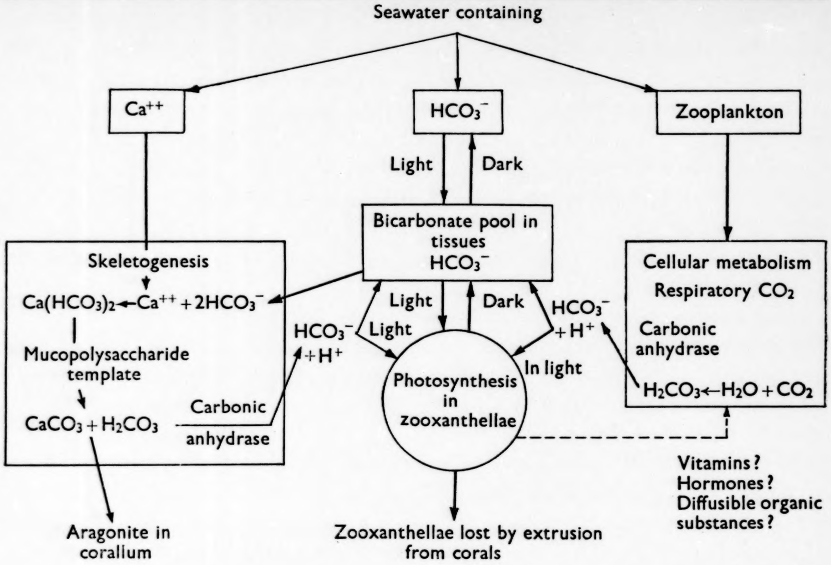
Seawater containing
Ca++
HCO3−
Zooplankton
Light
Dark
Bicarbonate pool in tissues HCO3−
Skeletogenesis
Ca(HCO3)2 ← Ca++ + 2HCO3−
Mucopolysaccharide template
CaCO3 + H2CO3
Carbonic anhydrase
HCO3− + H+
Light
Dark
Light
HCO3− + H+
In light
Photosynthesis in zooxanthellae
Cellular metabolism
Respiratory CO2
Carbonic anhydrase
H2CO3 ← H2O + CO2
Vitamins?
Hormones?
Diffusible organic substances?
Aragonite in corallium
Zooxanthellae lost by extrusion from corals

FIGURE 10 – *Possible pathways of calcification in relation to tissue respiration and photosynthesis by zooxanthellae in reef corals.*

The coral skeleton is also remarkable for being composed entirely of $CaCO_3$ with the crystalline structure of aragonite; calcite is completely absent. This probably has some important consequences with regard to the chemical composition of the corallum and the geographic distribution of the corals as a group. Since the skeleton is pure aragonite, magnesium carbonate is almost absent from the corallum, despite the fact that magnesium carbonate is more abundant in seawater than is calcium carbonate. Those calcareous organisms that deposit calcite as well as aragonite have at least ten times more $MgCO_3$ in their skeletons than the corals have [15]. H. Lowenstam has suggested [16] that the failure of corals to produce calcite may be the factor responsible for the marked reduction in the number of scleractinian species in cold waters compared with their abundance in warm waters. Organisms capable of producing both calcite and aragonite tend to deposit more of the former during cold seasons, and more of the latter during warm seasons. Since corals cannot substitute the less soluble calcite for aragonite in cold water, their calcification mechanism may become so inefficient as to hinder skeletogenesis under these conditions.

The application of tracer methods using stable isotopes has led to some important advances in our knowledge regarding the probable origin of the carbonate fraction of the coral limestone. It has been pointed out by a number of investigators [17–19] that the $^{18}O : ^{16}O$ and $^{13}C : ^{12}C$ ratios of the carbonate deposited by reef corals are not the same as in the carbonate dissolved in seawater. C. Emiliani [19] has suggested that the oxygen-isotope ratio might be altered if chemical exchange occurs between the oxygen that is liberated by zooxanthellae and the carbonate that is deposited. If the skeletal carbonate of the corals is derived from metabolism rather than from the seawater, then, again, alterations in the isotopic ratios are to be expected. Metabolic reactions produce isotopic fractionation because of the slightly different equilibrium-constants for different nuclides.

THE MECHANISM OF CALCIFICATION

The isotopic evidence for a metabolic origin of the skeletal carbonate agrees with our own experimental data; it is now possible to define some of the more probable pathways in the calcification process in corals. This is only a first approximation, a working hypothesis that may also find general application to processes of $CaCO_3$ deposition in the other calcareous organisms.

It appears (figure 10) that calcium is absorbed from the seawater as Ca^{++} and transferred by an as yet unknown mechanism to the site of calcification, which is probably localized just outside the calicoblastic epidermis. At this point the Ca^{++} is absorbed on a mucopolysaccharide-like material that forms part of the organic matrix and acts as the template upon which the initial stages of skeleton mineralization occur. Here the Ca^{++} combines with bicarbonate of primarily metabolic origin to form calcium bicarbonate and then calcium carbonate. The rate of calcium carbonate precipitation would, in principle, be governed by the overall rate of the coupled system

$$Ca^{++} + 2HCO_3^- \rightleftharpoons Ca(HCO_3)_2 \qquad (1)$$

$$Ca(HCO_3)_2 \rightleftharpoons CaCO_3 + H_2CO_3 \qquad (2)$$

$$H_2CO_3 \xrightleftharpoons{\text{carbonic anhydrase}} H^+ + HCO_3^- \qquad (3)$$

$$H_2CO_3 \xrightleftharpoons{\text{carbonic anhydrase}} CO_2 + H_2O \qquad (4)$$

at the site of mineralization. A crucial factor is the rate at which H_2CO_3 is removed from the system by reactions 3 or 4, both of which are catalysed by carbonic anhydrase. As tropical marine surface-waters are supersaturated with respect to $CaCO_3$, small changes in the velocity of reactions 3 and 4 will greatly increase the velocity of reactions 1 and 2. Under these conditions the free-energy changes are very small and the work done by coral in skeletogenesis is consequently also small. If the scheme is essentially correct, it is easy to see how the presence of photosynthesizing zooxanthellae causes such a marked increase in the growth rate of reef corals. Both CO_2 and HCO_3^- are fixed by algal photosynthesis. This would have the same effect as carbonic anhydrase in increasing the overall reaction-rate of the system. When reef corals are exposed to light, the zooxanthellae and carbonic anhydrase exert their effects synergically; in darkness only the latter can act.

CONCLUSIONS

Although there can now be little doubt that zooxanthellae assist coral skeletogenesis by a mechanism similar to the one outlined above, these symbionts probably have other important effects on the bio-economy of corals that cannot be fully described here. Their intimate structural relation to the coral host is shown in the electron-micrograph in figure 8. There is still a lively controversy between those who hold that the only function of the zooxanthellae is to supply the coral with oxygen and remove carbon dioxide [20], and those who believe that zooxanthellae are a source of food as well as of oxygen [21]. The writer favours the view that the zooxanthellae increase the metabolic efficiency of the animal host both through *in situ* production of oxygen and absorption of inorganic waste products by photosynthesis, and through the secretion of trace amounts of vitamin-like or hormone-like factors [3, 22]. The writer agrees with C. M. Yonge [23] that the zooxanthellae do not appear to be food for corals.

Apart from the problem of trophic relationships between the scleractinian corals and their algal symbionts, it is quite certain from our experimental evidence that, through their chemical potentiation of the calcification process, the zooxanthellae must have played a major role in the evolution and growth of shallow-water coral-reefs. The development of such enormous communities in the face of constant battering by heavy seas was possible only when processes of limestone deposition became fast enough for the rate of accumulation to exceed the rate of loss by organic and inorganic attrition. The synergistic effect of the zooxanthellae on the calcification rate of corals provided the necessary stimulus and was one of the decisive factors in the evolution of coral reefs.

ACKNOWLEDGMENTS

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The beginnings of phosphorus manufacture

Arthur Albright, who effectively started the British manufacture of phosphorus, was born 150 years ago. This is therefore an appropriate time at which to consider the history of the discovery and the early manufacture of this element.

Phosphorus was discovered by Hennig Brand, an alchemist and quack, in about 1670, when he was distilling human urine in an attempt to find a substance that would change silver into gold. (The carbon produced by the charring of the organic residue would act as a reducing agent for the phosphorus compounds normally present in urine.) The element—he called it *kaltes Feuer*—was a chemical curiosity, and Brand achieved a considerable social success as well as scientific fame. Johann Kunckel heard of the discovery and, together with his friend Johann Daniel Krafft, visited Brand. According to the generally accepted story, Brand would not say how he made phosphorus, and Kunckel had to rediscover the method. He also devised a method for casting phosphorus into sticks, and advertised it for medical use in his treatise on 'Phosphorus Mirabilis and its wonderful shining pills'. It was, however, Krafft who first demonstrated phosphorus in England, at the court of Charles II and also before the Royal Society. Boyle saw this demonstration, and wrote enthusiastically of the way that the 'twinkling sparks, without doing any harm to the Turkey Carpet they lay on, continued to shine for a good while'. Whether or not Boyle had again to rediscover the method of preparation is not certainly known; he himself stated that the only information that Krafft gave him was a hint stating that the 'principal matter' was 'somewhat that belonged to the body of man'. What is certain is that it was Boyle who first published the preparation of phosphorus as an aqueous solution or suspension, in his 'The Aerial Noctiluca' (1680), and as a solid, in 'The Icy Noctiluca' (1681–82); and he also first scientifically described the element and its properties.

Boyle's assistant, Ambrose Godfrey Hanckewitz, established himself as a pharmacist, under the name of Godfrey. He advertised the usual contemporary pharmaceuticals, such as smelling salts, Glauber's salt, balsams, and cordials, and also that he was 'the only one in London who makes inflammable phosphorus . . . All unadulterated, wholesale 50 shillings an ounce, and retail three pounds sterling an ounce'. Even at this price there was a ready market for phosphorus, and Godfrey travelled throughout Europe selling it, dying a rich man in 1741.

The high cost of phosphorus was due to the very poor yield of the process and remained high until Scheele, in 1777, devised a method of preparing it from bone-ash. The first commercial application of this process in Britain effectively dates from 1844, when Arthur Albright persuaded Edmund Sturge, with whom he had gone into partnership a few years earlier, to start making phosphorus. The firm was then at Selly Oak, Birmingham, but it shortly moved to Oldbury. The aim was to provide phosphorus for the British match trade; the native supplies at that time were very small indeed—about a ton a year—and a large amount had to be imported.

A French gelatine-making company, *La Société Vve. Dupasquier, fils et Coignet*, had started making phosphorus in 1838, and manufacture in Germany began at about the same time. Imports to Britain reached a peak value of over £2500 in 1844. When Albright decided to compete with the French firm, he had the disadvantage of having to import bones, but against this had what proved to be the decisive advantage of cheap coal. Black Country coal could be bought for one and sixpence a ton; it has been estimated that the French company was paying fifteen shillings a ton. Imports fell rapidly; by 1851 Britain was actually exporting phosphorus.

The usual raw material was bone-ash from South America, although Albright did make an adventurous trip to Galatz, on the Danube, in order to see whether he could use the residue from the slaughter-houses of the meat-canning industry that had been established there. It proved impossible to ship the bones before treatment, and he was forced to set up calcining furnaces on the spot. The bone-ash—in later years rock phosphates were used—was treated with sulphuric acid, and the resulting phosphoric acid was concentrated, mixed with charcoal, dried, and ground so as to be ready for the retorts. These retorts—bottle-shaped fireclay vessels about four feet long—were mounted in coal-fired furnaces in groups of twenty-four; they had iron necks that led the phosphorus vapour to the condensers. The distillation was continued for about sixteen hours; the phosphorus was condensed under water to prevent oxidation by the air, and was ladled off and allowed to set into thirty-pound cakes that were bleached with chromic acid. The bleached phosphorus was sent down a steam-jacketed cylinder to keep it molten, filtered through chamois leather, and cast into sticks.

Contemporary accounts give a vivid picture of British phosphorus-manufacture at that time. The phosphorus distillery of those days was a striking sight with 'long yellow flames' and with pieces of burning phosphorus 'spitting forth in fiery balls'; there was an incessant bubbling of the condensing phosphorus in the water basins, and an 'intolerable stench' of phosphorus derivatives. The combination of this factory with the adjacent Chance's soda-making factory, using the Leblanc process, with its vast output of offensive alkali-waste, must have contributed to turning Oldbury from what a local historian described as a pleasant and pretty place, nestling below the green slopes of Rowley Hills, into a waste, 'a town of unrelieved, almost defiant ugliness'.

Many improvements in manufacturing technique originated in this British factory. The wasteful directly heated furnaces were replaced by retorts fired by producer gas and using the Siemens regenerative principle; this principle was in fact used both here and in Chance's glass-works before it was widely adopted by steel manufacturers. These furnaces in turn gave way to electrical furnaces, which were continuous in operation; they depended on a process, that of preparing phosphorus by heating the bone-ash with silica (sand) and carbon, that had been proposed by Wöhler in 1829. The success of the process depends on attaining a temperature sufficiently high for the slag to be tapped off while molten. The first attempts to work it—by an Edinburgh man, J. B. Readman—used a blast furnace, but a sufficiently high temperature could not be attained with this. Blast furnaces were eventually used for phosphorus manufacture in the United States; even when the technical difficulties had been overcome it was found that they needed to be very large to be economically successful. Readman also took out a patent for a similar process using electrical heating, and this patent was taken up by the Electric Construction Company of Wolverhampton. This group formed the Phosphorus Company in 1890, and started operations using the electric furnace with two horizontal electrodes that is still frequently represented in textbooks of chemistry. This furnace is, in fact, obsolete, and was replaced by one of an improved design, using vertical electrodes, soon after the Albright company, by then Albright and Wilson, took over the firm.

Albright was deeply disturbed by the dangers to health and property that were involved in phosphorus manufacture. Yellow phosphorus, the allotrope prepared by all the processes so far mentioned and the one then used in matches, was both spontaneously inflammable and poisonous, causing a bone gangrene known as 'phossy jaw'. Anton Schrötter, of Vienna, had discovered in 1845 that a non-poisonous, stable, form, red phosphorus, could be made by heating yellow phosphorus in an inert atmosphere. The process could be explosive, as the reaction is exothermic, and he had decided that it had no commercial value.

In 1849 Schrötter was Albright's guest at a British Association meeting at which he read a paper on the new allotrope. Albright decided that the process was practicable, bought Schrötter's patent, and set to work to devise a way of avoiding explosions. He and Julius Lowe, one of his staff, designed a cast-iron pressure pot, having a small-bore tube as a safety valve, that eventually eliminated the risk of explosions. Albright then started a campaign to persuade European match manufacturers to use red phosphorus in the place of yellow.

It proved to be extremely difficult to make a satisfactory 'strike anywhere' match using red phosphorus: an alternative approach was to try to make matches using the 'safety-match' principle, in which all the phosphorus is on the box, none being incorporated in the head of the match. The first successful ones were made by the Lundström brothers of Sweden in 1855. They immediately ordered such a large quantity of red phosphorus that Albright imagined that it must be intended for making munitions and, as a Quaker, refused to supply them. He was, however, reassured, and sent the red phosphorus; the Lundström brothers started to manufacture matches on a large scale. This discovery of a satisfactory way of using red phosphorus for safety matches was the basis of the successes of both the Swedish match industry and Albright and Wilson, and it marked the beginning of the modern period of phosphorus manufacture and use.

Isotope separation by reversible chemical processes

E. GLUECKAUF

When the existence of isotopes was first recognized it was believed that, because of the identity of their electronic configurations, their separation was possible only by physical methods. The preparation of deuterium by electrolysis of water demonstrated that chemical methods of separation were also possible, and today chemical methods are not only widely used but are sometimes the method of choice. This article discusses the theoretical principles, and considers the advantages and limitations of chemical methods of isotope separation.

GENERAL CONSIDERATIONS

In recent years the uses of separated stable isotopes have become very varied. By far the largest number of all the separated products are used for studies of nuclear properties, but substantial use is made of them in the study of physico-chemical problems, for chemical analysis by the isotope-dilution technique, for medical and biological investigations, and as raw material for the preparation of radio-isotopes. But potentially valuable though they are, the difficulty of separating isotopes is a limiting factor in their use. To give a typical example, the radioactive isotope ^{47}Ca, with a half-life of 4·7 days, could, if readily available, be one of the most useful isotopes in the diagnosis of cancer. It can be produced by neutron irradiation of ^{46}Ca, a naturally occurring isotope; but though calcium is plentiful, the ^{46}Ca content of the natural element is only 32 parts per million, making its enrichment a difficult and expensive process, so that 1 mg of ^{46}Ca produced by electromagnetic separation may cost about £1000. This raises the question whether chemical methods of isotope separation might not prove cheaper than physical ones, and this question several institutions are attempting to answer.

As the result of the experiments in 1912–13 by F. A. Paneth in Vienna and G. de Hevesy in Manchester, both of whom demonstrated that Ra D (a lead isotope) and ordinary lead could not be separated by chemical methods, there was established a firm belief that isotopes show identical chemical behaviour and are therefore inseparable by chemical methods. In 1919 Lindemann (later Lord Cherwell) calculated that, in principle, isotopes must be separable, though the differences were so small that there would be little hope of success in practice. Throughout the 1920s many laboratories were studying methods of separation and achieved—mainly by distillation methods—minor changes in the isotopic ratios of elements such as neon, chlorine, zinc, and mercury. In 1932, however, H. C. Urey [3] showed that the electrolytic decomposition of water leads to a substantial enrichment of deuterium in the remaining fraction, and that repeated electrolysis could lead to essentially pure deuterium. Once it was realized that chemical methods could be utilized for isotopic separations, a large variety of methods was studied, and the fundamental techniques are now well understood. The quantities of isotopes now separated vary widely according to requirements; they range from grams per day for materials of interest for research—such as ^{10}B, ^{13}C, ^{15}N, ^{18}O—to kilograms per day for isotopes such as D and ^{235}U that are required for the atomic industries. ^{6}Li occupies an intermediate position.

Isotopic atoms have, of course, identical electronic configurations and therefore exhibit essentially the same chemical behaviour; they differ, however, in their atomic masses. In the case of the monatomic gases, this difference affects mainly the zero-point energies in the condensed phase, and the lighter isotope is therefore invariably more volatile. In the case of polyatomic molecules, however, vibration and rotation also contribute to the energy content, and may either reinforce or diminish the zero-point energy (that is, its internal energy at absolute zero); the combination in turn will affect volatility and thermodynamic activities. Thus, isotopic molecules, even if their molecular weight is the same—as in the case of HT and D_2—may differ appreciably in their vapour pressures at any given temperature (figure 1). The vibrational and rotational effects can more than counterbalance the mass effect; as has been shown by

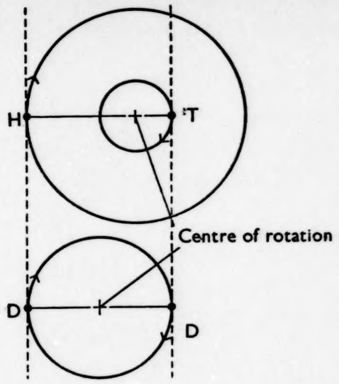

FIGURE 1 – *Effect of rotation of isotopic masses on molecular volume for HT and D_2.*

T. F. Johns, $^{12}C^{18}O$ is slightly more volatile than $^{13}C^{16}O$, even though the former is the heavier molecule [1*a*]. For example, at 60° K the ratio (α) of the vapour pressures of the two compounds is 1·0028; α is called the separation factor of the single-stage equilibrium. As isotopic mixtures are 'ideal solutions', the molar fractions (X) in the two phases of a vapour-liquid equilibrium are related by

$$\ln\left(\frac{X_1}{1-X_1}\cdot\frac{1-X_2}{X_2}\right)=\ln\alpha\simeq\alpha-1=\varepsilon$$

where ε is the separation parameter.

Isotope separation can in principle be achieved by two types of processes. These are respectively rate processes, in which one species reacts or diffuses faster than the other, usually as the result of a smaller mass, and equilibrium processes, in which one or the other species is thermodynamically favoured in one of the phases. To the first class belong separations by barrier diffusion, thermal diffusion, centrifugation, electrolysis, electro-migration, kinetic isotope effects, and, in a sense, even electromagnetic separation. To the second class belong distillation and chemical exchange reactions. When, as is usually the case, the difference of rate or equilibrium constants is only small, it is not possible to separate isotopes completely in a single operation; the operations may have to be repeated many times, in some cases thousands of times, before the desired degree of separation is achieved.

This need for repetition emphasizes one essential difference between rate processes and equilibrium processes. The former are irreversible reactions, and substantial amounts of energy have to be provided at every stage. The equilibrium processes, however, can be conducted in an almost reversible manner and, by making use of multi-stage counter-current processes, energy is required virtually only at the ends of the cycles. For comparable separations (that is with equal values of α), efficiently conducted equilibrium processes require only a very small fraction of the power required for rate processes.

It has been calculated that the minimum power-consumption W required to separate 1 mole of pure isotopic compound present originally at the molar fraction X is, for an irreversible process, $> 4RT/\varepsilon^2X$. With a reversible process, with n theoretical plates in each column, this value, according to H. London [1*b*], need be only about $5{\cdot}3\ RT/n\varepsilon^2X$ (where $n \leqslant 500$), that is to say, two orders of magnitude less for the same conditions. But separation factors are not in fact equal for the two types of processes, and for very heavy isotopic molecules or atoms, for example UF_6, the separation parameter for irreversible processes (such as diffusion) greatly exceeds that for reversible processes such as distillation (Table 1). For relatively light atoms and molecules, however, reversible chemical processes show separation factors that are of the same magnitude as those arising from irreversible processes, and it is here that their practical applications become important.

TABLE I

Isotopic species	Separation parameter ε	
	Distillation	Diffusion
H_2/HD	0·73	0·225
$^{10}BF_3/^{11}BF_3$.. ..	−0·0065	0·0074
$^{20}Ne/^{22}Ne$	0·0445	0·049
$^{16}O_2/^{16}O^{18}O$ ..	0·0052	0·030
$^{36}A/^{40}A$	0·006	0·055
$^{235}UF_6/^{238}UF_6$ ..	< 0·0001	0·0043

The best-known example of a multi-stage reversible chemical process is fractional distillation, which involves the repeated equilibration between a gaseous and a liquid phase. In this case the chemical species in the gaseous and liquid phases are the same, for example,

$$\underset{\text{Liquid}}{^{20}Ne} + \underset{\text{Gas}}{^{22}Ne} \overset{\varepsilon=0{\cdot}044}{\rightleftharpoons} \underset{\text{Gas}}{^{20}Ne} + \underset{\text{Liquid}}{^{22}Ne}$$

though their proportions in the two phases vary, and refluxing is obtained simply by boiling at the bottom and condensing at the top of the column.

If the exchanging species are not of the same chemical type we have a gas-liquid exchange reaction, such as

$$\underset{\text{Gas}}{^{14}NO} + \underset{\text{Soln.}}{H^{15}NO_3} \overset{\varepsilon=0{\cdot}055}{\rightleftharpoons} \underset{\text{Gas}}{^{15}NO} + \underset{\text{Soln.}}{H^{14}NO_3}$$

To reflux, it becomes necessary to convert the NO to HNO_3 at the top of the column and the HNO_3 to NO at the bottom, as is described in more detail later. In general, chemical exchange reactions have considerably higher separation factors than distillation. For the distillation of nitrogen isotopes, $\varepsilon = P(^{14}N^{14}N)/P(^{14}N^{15}N) - 1 = 0{\cdot}0062$ at 64·8° K; this compares with $\varepsilon = 0{\cdot}055$ for the chemical exchange described above.

Other reversible processes may involve two immiscible liquid phases—as in solvent extraction; alternatively, one of the phases may be solid—as in ion-exchange and gas chromatography, the second phase then being liquid or gaseous.

DISTILLATION

The most important factor for the separation is the single-stage separation factor (α) or, rather, the parameter $\varepsilon = \alpha - 1$. The important column characteristics—like size and cost, power consumption, and equilibrium time—all depend on ε^2. In the case of vapour-pressure equilibria, α is the ratio of the vapour pressures of the two isotopic species. The value of ε depends on the temperature; below 100° K it is usually proportional to $1/T^2$. As the separation effect of a single-stage equilibration is small, a reflux column is used as countercurrent cascade. For isotope separation the earlier type of column with bubble-caps is not very useful, because of the comparatively large height of the single stage and of its large retention of product. Columns filled with packing are nowadays employed, and this ensures continuous contact between the phases under more advantageous conditions. Such a column is considered to have *n* theoretical plates if its operation is equivalent to *n* successive equilibrations. The total change in isotopic concentration for a binary mixture, with molar fractions X and $(1 - X)$ of the two isomeric species, between the top (T) and the bottom (B) of such a column at total reflux is then given by

$$\frac{X_T}{X_B} \cdot \frac{1 - X_B}{1 - X_T} = \alpha^n = \exp(\varepsilon n) \quad \text{if } \varepsilon \ll 1$$

The number of theoretical plates required to give a desired enrichment is shown in Table II.

TABLE II

Number of theoretical plates (n) required for various enrichment factors (R) and separation factors (α), assuming total reflux

R = overall enrichment factor	10	100	1000	10000
α	*n*			
2·0	3	7	10·0	13
1·4	7	14	21	27
1·1	24	48	73	97
1·05	47	94	141	188
1·02	115	230	345	460
1·01	230	460	690	920
1·005	460	920	1380	1840

When product is withdrawn—even at a low rate—the enrichment is considerably lower. This is demonstrated [1*c*] in figure 2, which illustrates the isotopic enrichment of ^{10}B ($X_0 = 0{\cdot}2$, $\varepsilon = 0{\cdot}025$). X is the molar fraction of ^{10}B in the product, and the abscissa gives the withdrawal rate P/B, where P is the withdrawal ratio of product and B is the boil-up rate in the column. The diagram shows that even with an infinitely long column the withdrawal rate P/B must be kept below 0·5 per cent, or $< 0{\cdot}2\varepsilon$, if a high purity of product is to be achieved.

The height of a theoretical plate depends greatly on the type of packing, which must simultaneously offer a large area of contact to the gas stream and the smallest possible retention of liquid so that equilibrium is quickly obtained. Theoretically, the smallest plate-heights should be achieved with very narrow empty tubes, of 1–2 mm internal diameter, in which the liquid runs down the wall in a thin film. This should give plate-heights equal to the tube diameter. But there are considerable practical difficulties in the use of such narrow wetted-wall columns; in particular the throughput is very low. This makes it necessary to use as many as 100 tubes in parallel if useful amounts of product are to be obtained [2]. For laboratory work it is more practical to employ wider tubes filled with a small random packing. By using cylindrically rolled wire netting—such as Dixon gauze packings (figure 4), which also give a low pressure-drop per plate—the height of a theoretical plate can be kept as low as 1 cm in

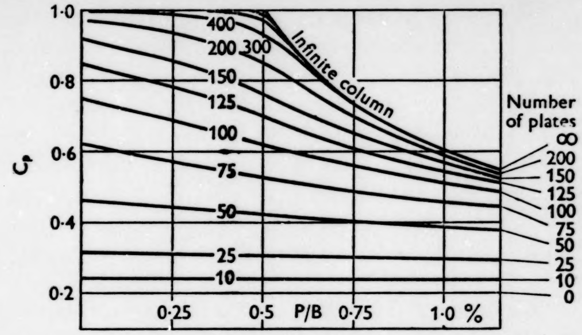

FIGURE 2 – *The effect of the withdrawal rate (P/B) on* ^{10}B *content of the product* (C_p) *during separation of boron isotopes* ($\varepsilon = 0{\cdot}025$).

small-diameter columns. For very large industrial columns, however, it is more economical to use expanded perforated metal sheet such as Spraypak (figure 5) or Panapak; though giving theoretical plate heights of about 45 cm, these allow much greater throughputs.

An interesting example of isotope separation by distillation is the production of heavy oxygen (^{17}O and ^{18}O) from water by I. Dostrovsky and A. Raviv [*1g*] at the Weizmann Institute of Science in Israel. Of these isotopes, the rare ^{17}O—which is contained in natural oxygen only to the extent of 0·037 per cent—is of particular interest, because its nuclear magnetic resonance is such as to permit non-destructive analysis, so opening up large fields of tracer application, particularly in biology and medicine. As the separation factor diminishes with increasing temperature, the distillation is carried out at reduced pressure and temperature. The plant operates in two stages. A pre-enrichment section, consisting of several four-inch columns 30 ft in length operating in parallel, produces an enriched product. This is then fed into a cascade of five columns, two of which are for stripping and three for further enrichment. This cascade represents more than 2000 theoretical plates, and the apparatus produces approximately 10 g per day of highly enriched $H_2{}^{18}O$.

EXCHANGE DISTILLATION

An interesting variation of the ordinary distillation process is the so-called exchange distillation, which can be employed if a liquid compound is dissociated in the gaseous phase, for example,

$$BF_3(C_2H_5)_2O \rightleftharpoons BF_3 + (C_2H_5)_2O$$

Here the factor which leads to the isotopic enrichment is not the difference between the vapour pressures of the compounds but the exchange reaction between gaseous BF_3 and the liquid $BF_3(C_2H_5)_2O$ complex:

$$^{10}BF_3(C_2H_5)_2O + {}^{11}BF_3 \rightleftharpoons {}^{11}BF_3(C_2H_5)_2O + {}^{10}BF_3$$

This combines the operational simplicity of a distillation process with the advantage of the considerably larger separation factor of the chemical exchange ($\varepsilon = 0{\cdot}034$ instead of 0·0075 as for distillation of BF_3). The method was first used in the United States in 1943, but details were not released until its rediscovery in Britain, Sweden, and Yugoslavia, independently, in 1957 [1]. The process is used technically for producing ^{10}B, for example, for neutron counters. A column operating in England contains about 400 theoretical plates and enriches ^{10}B, in kg quantities, from its natural content of 20 per cent to 96 per cent [*1c*].

In other examples of exchange distillation, the dissociation of trimethylamine acetate and of aqueous ammonium carbamate have been employed. The reactions are respectively:

$$CH_3.COONH(CH_3)_3 \rightleftharpoons N(CH_3)_3 + CH_3COOH$$
$$(\varepsilon = 0{\cdot}012 \text{ for } {}^{15}N \text{ enrichment})$$
$$NH_2.COONH_4(aq) \rightleftharpoons CO_2 + 2NH_3$$

In the second example both ^{15}N ($\varepsilon = 0{\cdot}015$–$0{\cdot}020$) and ^{14}C are enriched. In the case of the exchange distillation of BF_3-methyl-ether one finds in addition to the ^{10}B enrichment also a small enrichment of ^{18}O, arising from the exchange of the liquid compound with the gaseous ether ($\varepsilon = 0{\cdot}012$).

CHEMICAL EXCHANGE (GAS-LIQUID)

This method of isotope separation was first suggested in 1935 by H. C. Urey and L. J. Greiff, and led to the first 'large-scale' enrichment of ^{15}N, utilizing the exchange of gaseous NH_3 with solutions of ammonium salts ($\alpha = 1{\cdot}031$). The most elegant example of this type of process is, however, the exchange of HNO_3 with NO utilized by T. I. Taylor and W. Spindel in 1955 [*1d*], which also has a considerably larger separation factor. Using this process, L. Gowland and T. F. Johns [4] designed a cascade with two 15 ft columns in series, with a total of 300 theoretical plates, which enriched 0·4 g per day of ^{15}N from its natural concentration of 0·36 per cent to a purity of 99·8 per cent. An interesting point of their design was that it was fully automatic and did not involve the use of pumps or electronic devices. Each column had a refluxer at its base in which the nitric acid was converted to nitric oxide by means of sulphur dioxide, and a top refluxer where the nitric oxide was reconverted

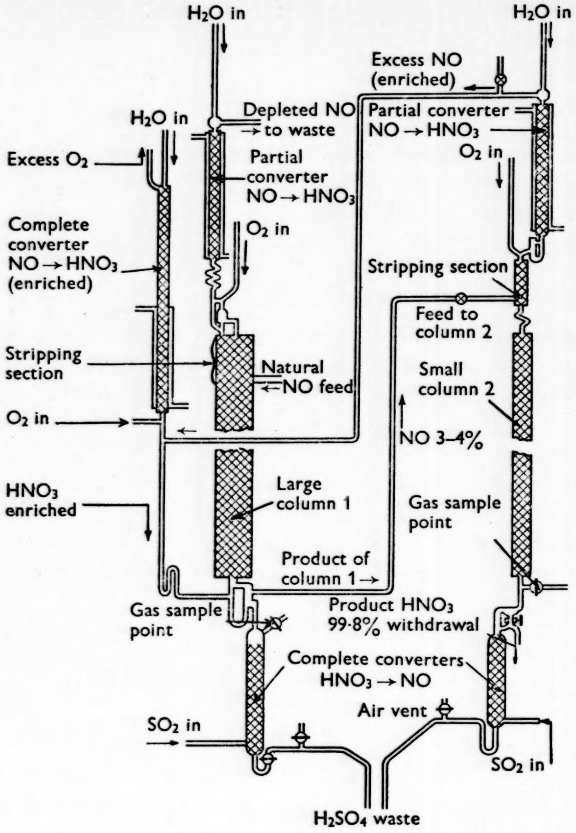
H₂O in
H₂O in
Excess NO (enriched)
H₂O in
Depleted NO → to waste
Partial converter NO → HNO₃
Excess O₂
Partial converter NO → HNO₃
O₂ in
Complete converter NO → HNO₃ (enriched)
O₂ in
Stripping section
Feed to column 2
Stripping section
Natural ← NO feed
Small column 2
O₂ in
NO 3–4%
HNO₃ enriched
Large column 1
Gas sample point
Product of column 1 →
Gas sample point
Product HNO₃ 99·8% withdrawal
Complete converters HNO₃ → NO
Air vent
SO₂ in
SO₂ in
H₂SO₄ waste

FIGURE 3 – *Scheme of nitrogen isotope separation plant by Gowland and Johns. The arrangement is of particular interest because it uses two columns in series without the use of pumps.*

to nitric acid by combination with oxygen and water. The reflux ratio at the top of the columns could be adjusted simply by regulating the oxygen flow. As all transport between the columns took place via the gas phase, under pressure of the gases (figure 3), no pumps were required for either liquids or gases: this greatly increased the reliability of operation. The waste nitric oxide from the top of the second column was completely converted to nitric acid in an extra converter, and this still-enriched material was fed back to the first column.

Other chemical-exchange reactions with useful separation factors (at 25° C) are

$$S^{16}O_2 + 2H_2{}^{18}O \rightleftharpoons S^{18}O_2 + 2H_2{}^{16}O \qquad (\alpha = 1{\cdot}020)$$
$$C^{16}O_2 + 2H_2{}^{18}O \rightleftharpoons C^{18}O_2 + 2H_2{}^{16}O \qquad (\alpha = 1{\cdot}044)$$
$$^{13}CO_2 + H^{12}CO_3{}^- \rightleftharpoons {}^{12}CO_2 + H^{13}CO_3{}^- \qquad (\alpha = 1{\cdot}012)$$
$$H^{13}CN + {}^{12}CN^- \rightleftharpoons H^{12}CN + {}^{13}CN^- \qquad (\alpha = 1{\cdot}012)$$
$$^{34}SO_2 + H^{32}SO_3{}^- \rightleftharpoons {}^{32}SO_2 + H^{34}SO_3{}^- \qquad (\alpha = 1{\cdot}019)$$
$$^{36}SO_2 + H^{32}SO_3{}^- \rightleftharpoons {}^{32}SO_2 + H^{36}SO_3{}^- \qquad (\alpha = 1{\cdot}040)$$

The design of chemical-exchange plants is very similar to that of distillation columns; Dixon rings and Helipak are usually the packing materials, giving the smallest theoretical-plate heights that can be attained. However, these heights never attain the small values obtained in the same columns for a distillation process. The reason for this is that the diffusion transport in the liquid phase—usually a solution of the exchanging molecule in water—is smaller by approximately an order of magnitude than in a pure liquid; also, the chemical exchange is often far from instantaneous.

CHEMICAL EXCHANGE BETWEEN TWO LIQUID PHASES

Isotope-separation processes involving equilibrium between two immiscible liquid phases are comparatively rare. Attempts in the author's laboratories to separate the lithium isotopes by exchange between a concentrated aqueous solution and a solution in tributyl phosphate did not show a significant separation factor. One case that has been described in the literature is the exchange of lithium between its liquid amalgam and various organic solutions. Thus G. M. Lewis and R. T. McDonald have investigated the amalgam exchange with solutions of lithium chloride in absolute ethyl alcohol and of lithium bromide in an alcohol-dioxan mixture. Reflux at the bottom of the column was produced by treating the lithium amalgam with alcoholic hydrochloric acid, thus transferring the lithium quantitatively into a neutral organic solution. Using an 18-metre glass column, they changed the $^7Li/^6Li$ ratio from 11·6 at the top (feed-point) to 5·5; their data do not permit a calculation of the single-stage separation factor [5]. However, a more recent report by L. Perret, L. Rozaud, and E. Saito [6] gives the single-stage separation factor between Li-amalgam and a solution of lithium bromide in dimethylformamide as approximately 1·05, and the values of α for other organic solvents may be expected to be very similar.

DUAL-TEMPERATURE CHEMICAL EXCHANGE

In the processes described so far—using distillation or exchange—reflux could be obtained either by condensation or by simple chemical processes. But in a number of exchange reactions, which are otherwise very useful for isotopic enrichment, no such simple refluxing process is possible. A typical case is

$$HOH + HSD \rightleftharpoons HOD + HSH$$

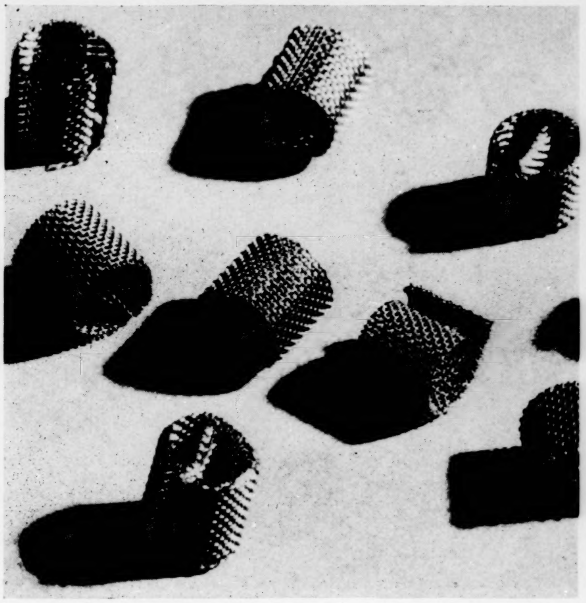

FIGURE 4 – *Dixon or Lessing gauze rings are among the most efficient packing materials for laboratory or pilot plant columns.*

FIGURE 5 – *Spraypak is one of the most efficient packing materials for large-scale columns for bringing liquids and gases into intimate contact.*

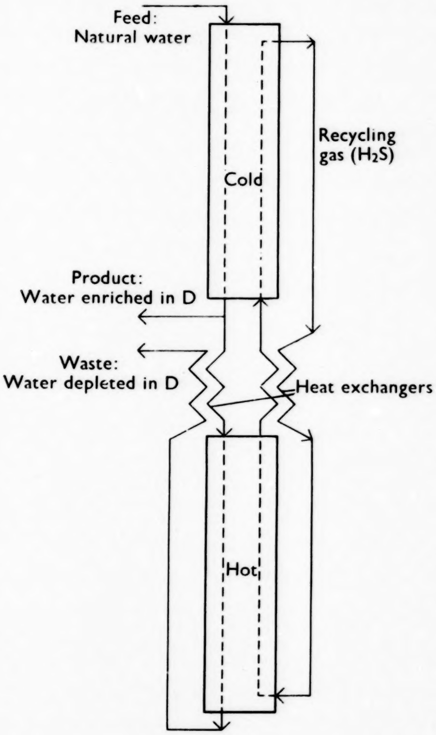

FIGURE 6 – *Schematic representation of dual-temperature chemical exchange process, for cases where conversion of one chemical species into the other at the refluxing ends of the column is not practicable.*

which requires at both ends of the column the complete conversion of hydrogen from H_2S to H_2O and *vice versa.*

In these cases, the refluxing action can be provided by a second column, running at a higher temperature (with a correspondingly lower value of α) which provides the enriched H_2S; this is fed against the current of H_2O into the enrichment end of the 'cold' column (figure 6). A simplified scheme can be visualized in which water of natural D_2O content (0·0145 per cent) is fed into the top of the cold column, which at 30° C has an effective separation factor $\alpha = 2{\cdot}27$; the waste, with reduced D_2O content, is withdrawn from the bottom of the hot column, which, at 130° C for example, has an effective separation factor $\alpha = 1{\cdot}65$. The actual equilibrium constants are somewhat different, because the separation factor is modified by the presence of steam in the gas phase, largely H_2S, and by the solubility of H_2S in water. Enriched product is withdrawn, as water, between the two columns. In practice, several dual-temperature systems are coupled in series, the depleted waste from the second system being returned to the first one. Generally, a product containing 10–20 per cent of D_2O is produced by this method, and this is finally concentrated by other methods, for example electrolysis or distillation.

This process, patented by J. S. Spevack [7] though proposed independently by Rideal and by

Harteck and Suess, was primarily designed for production of deuterium on the largest scale, for use in heavy-water reactors. It is very economical in power consumption, the demand arising mainly from the pumping power required to circulate the liquid and gas and the heat required to humidify the gas stream when entering the hot column. The energy required for heating the gas and liquid before they go into the hot column is largely recovered by heat exchange with these fluids when they leave the hot column. The temperature of the cold tower must be above 29° C, as otherwise H_2S forms a solid hydrate; that of the hot tower should be below 130° C, as otherwise the proportion of steam in the H_2S phase would become too high, which would adversely affect the separation process and the power consumption.

Similar dual-temperature processes have been proposed using the exchange of liquid H_2S with liquid H_2O; for the exchange of gaseous hydrogen with liquid NH_3, with potassamide as a catalyst [1*e*]; and for the exchange of gaseous hydrogen with water, using suspensions of platinum and carbon as exchange catalysts.

Though there would appear to be a wide field of application for dual-temperature processes, there are in fact severe practical limitations. The ratio of the mass-flows in the gaseous and liquid cycles must lie between the values of α at the two temperatures, and for all but the largest separation factors this entails a difficult control of the flow ratio.

CHROMATOGRAPHIC SEPARATIONS

While counter-current exchanges with two fluid phases (gas-liquid or liquid-liquid) have found application on the largest scale, the use of chromatographic processes, that is of exchangers involving one solid and one fluid (gas or liquid) phase, has not led to large-scale technical applications in isotope separation, although several interesting scientific investigations have resulted from them.

A priori, one would have thought that chromatographic methods would be very useful for isotope separations, because of the very small plate-heights (< 1 mm) that can be achieved in such columns. This would make it possible, without much expense, to operate with 10 000 and more theoretical plates in a single column as compared with the 500-odd theoretical plates that the best distillation column can provide. This advantage however, is more than offset by the extreme slowness with which equilibria that involve exchange between a solid and a liquid phase are attained, and by the very small number of gas-solid exchanges that give a reasonable separation factor.

The reactions involving a liquid phase can be subdivided into two groups:

1. Straightforward ion-exchange chromatography between an electrolyte solution and a solid ion-exchanger. Here the separation factors observed are all exceedingly small. Even for the most favourable case of $^6Li/^7Li$ the observed values of ε lie between 0·0010 and 0·0038, rising with the degree of cross-linking of the exchanger [8]. When we come to heavier ions, such as sodium, values around 0·0001 have been observed [9] for the exchange of ^{22}Na and ^{24}Na.
2. Exchange between the ions in the exchanger and an associated compound in the aqueous phase. The best-known example of this type is the enrichment of ^{15}N obtained by F. H. Spedding, J. E. Powell, and H. J. Svec [10], who used the equilibrium

$$NH_4^+ \text{ (exchanger) } \overset{\varepsilon=0\cdot026}{\rightleftharpoons} NH_4OH(aq)$$

After recycling a band of NH_4^+ through a series of 10 ft columns, so that the band travelled through a total length of more than 300 ft, they were able to produce, from a starting material with the natural ratio of $^{15}N/^{14}N = 0\cdot0036$, a small amount of enriched material containing 45 per cent ^{15}N.

The exchange reaction effective for the isotope separation is in this case not the ion exchange (which has a negligible separation factor) but the aqueous-solution equilibrium

$$[NH_4^+](aq) + [OH]^- \rightleftharpoons NH_4OH$$

The function of the exchanger is merely to hold back the ions while the solution containing the undissociated ammonia moves on.

A similar effect was observed by Japanese workers [11] for the passage of boric acid over anion exchanger. Here the effective equilibrium is the first dissociation of the boric acid in the aqueous solution:

$$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$$

For the $^{10}B/^{11}B$ exchange this gives a value of ε between 0·010 and 0·016. Again the exchanger serves merely to separate the ionic and non-ionic species from each other and so to produce the multi-stage effect.

In the case of gas chromatography, separation factors differ considerably according to the nature of the adsorption process involved. Utilizing physical adsorption, only very small values of ε have been observed: for example, for the separation of the neon isotopes with charcoal columns at liquid-nitrogen temperature ($\varepsilon = 0{\cdot}0020$) [12]. However, the untried case of $^3He/^4He$ might well give good separations, if adsorption on a charcoal column at liquid-hydrogen temperature is employed, as a result of the large mass-ratio of the isotopes and of the low temperature of separation.

If chemical adsorption is utilized, as in the gas-chromatographic separation of the hydrogen isotopes on palladium columns by E. Glueckauf and G. P. Kitt [1*f*], very large separation factors arise: for example, $\alpha = 1{\cdot}8$ for H—D and $\alpha = 2{\cdot}6$ for H—T mixture. The attainment of local equilibrium is fast, and, consequently, quick and efficient separations can be carried out; enrichment by a factor of 100 is easily obtained for substantial quantities of material.

If one is interested only in the heavier hydrogen isotope, it is enough to fill about a third to a half of the column with the isotopic mixture and then to push this band through the column either with further quantities of ordinary hydrogen or by progressively heating the column from the rear. As deuterium or tritium are less readily adsorbed on palladium than is hydrogen, they form a frontal band of high purity that can easily be separated from the rest. The sharpness of the separated bands can be seen from figure 7.

Unfortunately, the method is not economical for large-scale production of deuterium, where not simplicity but power consumption becomes the important factor. This is partly because of the high heat of adsorption of hydrogen on palladium, heat that has to be supplied for the regeneration of the column. A contributory factor is the use of gaseous hydrogen as the starting material; this is rather more expensive than the water used for the H_2S process described above. But for the reconcentration of litre quantities of dilute deuterium or tritium mixtures the method is unchallenged, and very much cheaper than, for example, thermal diffusion methods.

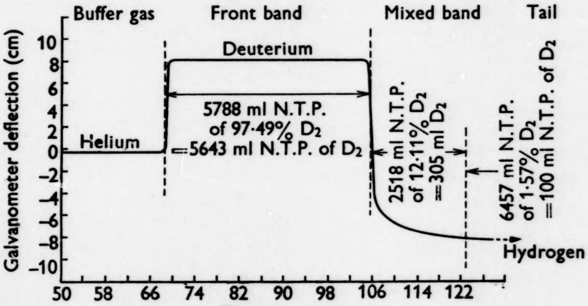

FIGURE 7 – *The chromatographic separation of hydrogen isotopes on a column containing 460 g of palladium powder. The graph gives the catharometer deflections of the eluted gas: first the helium buffer gas originally in the column, then the deuterium fraction, followed by the hydrogen fraction.*

CONCLUSION

As the chemical properties of different elements vary widely, so also do the chemical methods appropriate for separating them into their isotopes. Table III gives a short survey of the most promising methods that can be used for the lighter isotopes, excluding hydrogen; most of these have been tested either by laboratory methods or on a considerable scale. In the case of the hydrogen isotopes, the separation factors are so large that a variety of methods are possible; the choice will then depend on the quantities required, the available starting product (H_2, NH_3, or H_2O), and a number of economic factors.

Above an atomic weight of 40, chemical isotope

TABLE III

Element	Most promising method of isotope separation	α
$^3He/^4He$	Small-scale gas chromatography on charcoal cooled with liquid H_2	Unknown
$^6Li/^7Li$	Liquid-liquid chemical exchange between Li-amalgam and, for example, solution of dimethyl formamide in $LiBr_2$	1·05
$^{10}B/^{11}B$	Exchange distillation $BF_3 \rightleftharpoons BF_3(C_2H_5)_2O$	1·027
$^{13}C/^{12}C$	Distillation of CO	1·011
	Chemical exchange between HCN and CN^- (gas-liquid)	1·012
$^{15}N/^{14}N$	Chemical exchange (gas-liquid) $NO \rightleftharpoons HNO_3$	1·055
$^{18}O/^{16}O$	Distillation of NO or H_2O or CO	1·046 1·006 1·0076
$^{22}Ne/^{20}Ne$	Distillation of Ne	1·044
$^{34}S/^{32}S$ $^{36}S/^{32}S$	Chemical exchange (gas-liquid) between SO_2 and HSO_3^-	1·019 1·040
$^{36}A/^{40}A$	Distillation	1·006

separation is—at least at present—inferior to physical methods such as electromagnetic separation and diffusion. This inferiority is due both to the smallness of the chemical separation factors, which fall off rapidly with increasing atomic number and to the lack of pairs of compounds in which the chemical bond is sufficiently different and which also rapidly establish equilibrium with each other; this lack is particularly felt in the case of the metallic elements.

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PHYSICS

A Physics Anthology, *edited by N. Clarke. Pp. viii + 323. Published on behalf of the Institute of Physics by Chapman and Hall Ltd, London; Reinhold Publishing Corp., New York.* 1960. 35*s. net.*

This book consists of twenty-two articles published in the 'Bulletin' of the Institute of Physics and mostly based on lectures and addresses delivered at meetings organized by the Institute. It concludes with a report of a discussion dealing with 'Ethics and the Scientist' that was held in Manchester in 1956. Considerations of space will not allow even a list of the distinguished men responsible for the contributions nor of their individual subjects, which cover a wide field. A number of the contributions deal with physics as a factor in education and with the education of physicists; others deal with different aspects of physics in relation to industry; others again with the history of the subject, in particular two articles on Newton and Max Planck. They are all written by experts, some of them world-famous, with excellent powers of exposition. The collection should have a wide appeal.

It is worthy of special note that the book opens with an address by Sir Cyril Hinshelwood on 'Physics among the Sciences', written with characteristic conciseness, charm, and insight. This contains the sentence: 'What any man may believe about the ultimate purpose of existence can be little affected by his status in the world of space time', leading to the point that relativity has nothing to do with religion. Canon Raven, however, in an article on 'The Impact of Physics on Science and Religion', seems to imply that Einstein's theory of relativity had a profound influence on the religious and philosophic outlook. Perhaps Einstein may be allowed a word on the subject. It is authoritatively recorded that the Archbishop of Canterbury asked him whether he thought that his theory had any religious application and that the reply was a blunt 'None'. This is an example of how great men of science disclaim for their work the implications that theologians find in it.

E. N. DA C. ANDRADE

CONDUCTION IN SOLIDS

Electrons and Phonons; The Theory of Transport Phenomena in Solids, *by J. M. Ziman. Pp. xiv + 554. Clarendon Press, Oxford; Oxford University Press, London.* 1960. 84*s. net.*

When electricity travels through a solid it is transferred, in most cases, by electrons that move through the solid. Heat is in the main transferred by small-scale mechanical vibrations; in solids that conduct electricity, heat is also carried by the electrons. These phenomena require the quantum theory for their proper understanding, and one of its main consequences is that vibrational energy occurs in quanta. These behave in such a way that it is convenient to apply the language of particles to them, and to give them a name of their own, phonons. The theory of electrical and thermal conduction is thus largely concerned with the behaviour of electrons and phonons. These have many common features, and this fact makes a unified treatment illuminating.

In this book Dr Ziman sets out to explain the theory of transport phenomena in solids in a way that stresses the physical principles. He makes no pretence that the theory is everywhere on a rigorous footing. Rather, he exposes every dubious assumption for what it is, and leaves one to appreciate more clearly the foundations on which such an elaborate edifice has been built. He covers all the major aspects of conduction in solids, and deserves our gratitude for collecting in one place so much that would otherwise be difficult to find. The book is very readable; whenever the argument is going to run into turgid mathematics, Dr Ziman is at pains to give a sketch-map of the forest of his argument before we get lost in what he calls the undergrowth of suffixes. M. H. L. PRYCE

INORGANIC CHEMISTRY

Modern Aspects of Inorganic Chemistry (*third edition*), *by H. J. Emeléus and J. S. Anderson. Pp. xi+611. Routledge and Kegan Paul Ltd, London.* 1960. 35*s. net.*

This book needs no introduction to chemists, most of whom are already greatly indebted to the authors for an important part of their chemical education. Interest in this revised edition—which has largely been rewritten and reset—naturally centres around the changes that the authors have made. Their task of selection is not an easy one, as there has been so much rapid development in inorganic chemistry during the past decade.

There has been only a modest increase (about 10 per cent) in size, and the authors are to be complimented on their choice of material for deletion and addition. Under the heading 'π-Bonded Complexes' there is an up to date discussion of carbonyls, nitrosyls, cyclopentadiene complexes, and metal-aromatic complexes generally. The rapidly developing subject of inorganic-reaction mechanisms receives full attention. The discussion of modern valency-theory has been extended to include ligand field-theory and a little more on the molecular-orbital approach. The discussion of bonding in metal complexes embraces most recent developments.

This book should be in the hands of every teacher of chemistry and will do much to encourage the modern physical approach to the subject. So far as its value to the undergraduate is concerned it should be prescribed reading—I cannot give higher praise than to say that it is as good as before, but more up to date.

The authors have done an excellent job, and it is fitting to compliment the publishers on the fact that the price is still the same as that of the 1952 edition. R. S. NYHOLM

ORGANIC CHEMISTRY

Advances in Organic Chemistry: Methods and Results, *Vol. I, edited by R. A. Raphael, E. C. Taylor, and H. Wynberg. Pp. ix+387. Interscience Publishers Inc., New York; Interscience Publishers Ltd, London.* 1960. 90*s. net.*

This volume is the first of a new series which, according to the general introduction, will contain 'articles providing a critical appraisal and evaluation of new aspects ripe for further development and of novel extensions to well established methods'. The contents of volume I are: the Kolbe electrolytic synthesis (B. C. L. Weedon); polyphosphoric acid as a reagent in organic chemistry (F. Uhlig and H. R. Snyder); the Wittig reaction (S. Trippett); hydroxylation methods (F. D. Gunstone); the selective degradation of proteins (E. O. P. Thompson); and optical rotatory dispersion and the study of organic structures (W. Klyne).

Although most of the topics in this volume have already been reviewed at least once in the last five years, the scope and treatment of the first four topics are different from those of any previous reviews and are comparable with those that appear in *Angewandte Chemie*. They include examples of typical experimental procedures. The last two articles, occupying more than half the book, describe the very great progress made in these subjects during the last few years. The new series is welcome, and can be recommended to all organic chemists. J. F. W. McOMIE

SALT MARSHES

Salt Marshes and Salt Deserts of the World, *by V. J. Chapman. Pp. xvi+392. Leonard Hill (Books) Ltd, London; Interscience Publishers Inc., New York.* 1960. 95*s. net.*

Professor Chapman has successfully integrated many important studies on the physiography and vegetation of salt marshes and alkali deserts. Saline habitats, with the exception of mangrove swamps, are treated on a world scale.

The author's survey falls into three main parts: the first deals with the characteristics, formation, and ecological factors of salt marshes and inland salt deserts; the second with their vegetation; and the third with the physiology and biology of halophytes. Successional relations of the vegetation are summarized in many useful schemes, possibly somewhat dogmatically in view of the conjectural nature of the relationships in at least some of the areas. There are interesting sections on life-form analysis and on the biogeographical relationships of salt-marsh plants. The algal communities are given special attention.

This monograph should serve both as a source of information, and as a stimulant, to those studying salt-marsh vegetation. The book is abundantly illustrated and adequately documented, although more explicit legends to some of the figures and tables would help the reader. The photographs are a pleasing feature. A. J. WILLIS

GEOLOGY

Lead Isotopes in Geology, *by R. D. Russell and R. M. Farquhar. Pp. viii+243. Interscience Publishers Inc., New York; Interscience Publishers Ltd, London.* 1960. 65*s. net.*

It is now well known that it is possible to estimate the age of the earth's crust with some approach to precision by using the isotopic constitution of lead from galena and other sources, and that in favourable cases the approximate ages of lead-ore deposits can be determined. Some guidance is also afforded in unravelling the more complex ancestry of ores containing anomalous leads, that is those with an excess or deficiency of radiogenic lead relative to their ages. The authors of this most useful monograph are to be congratulated on their enterprise and success in bringing together in an attractive and easily accessible form all the information now available—hitherto widely scattered and in part previously unpublished—on a subject that has far-reaching applications in geology and geochemistry. After a general introduction, the successive chapters deal with methods, age of the earth, dating galenas, anomalous leads, case histories, extensions of the Holmes-Houtermans model, and lead-uranium-thorium methods. Tables of data, constants, and functions required for various calculations are given. The authors favour the hypothesis that the source of lead for lead ores is the earth's mantle, and that the lead has been carried to the surface, probably by volcanoes during the processes of continent formation; but they recognize that there are objections to this view and the model based on it, and in practice they deal quite fairly with all the models so far proposed. No one has yet given sufficient attention to the mixing and differentiating consequences of erosion, geosynclinal sedimentation, and subsequent granitization. A particularly useful feature is the appendix, which comprises several hundred isotopic analyses of common leads.

ARTHUR HOLMES

CYBERNETICS

Design for a Brain (*second edition, revised*), *by W. Ross Ashby. Pp. ix+286. Chapman and Hall Ltd, London.* 1960. *42s. net.*

Dr Ashby has added as a subtitle to the new edition of his book, 'The origin of adaptive behaviour'. 'Origin' may seem to the biologist rather ambitious, as the author deals hardly at all with the variety of organisms. What he does is to discuss the logic of 'trial and error machines', a subject that is obviously of the greatest biological interest. The novelty of his contribution is that he tries to show how trial and error, working through a series of 'step functions', makes possible even the highest activities of the nervous system. Indeed, he believes that trial and error is the necessary process that alone is capable of eliciting from the environment the information that is required for homeostasis. He is not disposed to look very closely for the actual origin of the variety that he postulates. He hints that the various steps may be found among unspecified events, at the molecular level, in neurons.

Not all biologists will readily follow the logic of Dr Ashby's proofs, but perhaps those least inclined to do so could learn most from attempting it. Biological problems involve many concepts that are difficult to make precise: one such is adaptation. We should be grateful to those who are prepared to do the hard thinking that is needed. The illustration of Dr Ashby's concepts is drawn, in the main, not from actual living organisms but from the model he has built, the homeostat. It is disappointing that the curves he provides from the working of this machine are the same in the second edition as the first. He does not seem to have been able to draw further information from it in the intervening seven years. We need an analogue that will compute continually for us parameters that we need to know—in fact, one that works as the brain does. In the meantime, Dr Ashby's analysis may encourage us to look at neural mechanisms with less rigid preconceptions as to what the significant variables may be.

J. Z. YOUNG

REPRODUCTION AND FERTILITY

Journal of Reproduction and Fertility, *Vol.* 1, *No.* 1, *February* 1960, *edited by C. K. Austin. Pp.* 120. *Blackwell Scientific Publications, Oxford. Quarterly, 20s. net; annual subscription, 70s. net.*

The promoters of the 'Journal of Reproduction and Fertility' are to be congratulated on the first number, which contains many interesting papers. There is an important article on phospholipids in mammalian semen, by Hartree and Mann. This subject has been confused for some time so far as mammalian spermatozoa are concerned: Hartree and Mann's clarification of the situation is therefore of special interest. Beatty's paper on the fertilizing capacity of semen obtained from different rabbits is also important; it is particularly welcome as a continuation and clarification of Russian work on heterospermic insemination. Bruce's paper on the effect of strange male mice in inhibiting pregnancy is of unusual interest. Clinicians and research workers in reproduction and gametology will value the possibility they now have of reading papers in their own fields in one journal, instead of in ten or more.

I hope the editors will publish papers on reproduction and gametology in plants and in animals other than mammals, because much was learned and is still to be learned from such studies. There is a tendency for the mammalian gametologist to pay too little attention to his invertebrate and botanical counterparts, and *vice versa.*

ROTHSCHILD

GENETICS

Human Biochemical Genetics, *by H. Harris. Pp. viii+310. Cambridge University Press, London.* 1959. *37s. 6d. net.*

In his book Dr Harris presents an admirable account of the remarkable advances in the study of human biochemical genetics since the publication of the second edition of Garrod's 'Inborn errors of metabolism' in 1923. He has condensed in an orderly and coherent manner information that is scattered throughout the literature. He starts off with two useful chapters in which, besides emphasizing the value of Garrod's concept of the biochemical defect, he recalls the basic ideas of genetics and provides a mathematical background to population genetics. Subsequently he discusses, mainly from a biochemical viewpoint, the well recognized and newly discovered normal and abnormal variations of the metabolism of amino-acids, carbohydrates, and other substances, and of the constitution of blood. The two chapters on human haemoglobins and blood-group substances are outstanding for their clarity. Except on appropriate occasions he avoids speculative or provocative parts of the subject, and also avoids mentioning species other than man, although he carefully indicates the weaknesses of accepted views and the problems yet to be answered. With this mode of approach, and with an ability to write clearly and concisely, he has produced a readable book, which is as up to date in its information as the speed of publication will allow.

J. R. P. O'BRIEN

ECOLOGY

The Biology of Weeds, *edited by J. L. Harper. Pp. xv+256. Blackwell Scientific Publications, Oxford.* 1960. *42s. net.*

For many years there has been a scarcity of books dealing with the biological side of weed studies as compared to the mass of literature dealing with their control; possibly weeds were not considered respectable for academic work. This volume will help to correct the position: it is a record of some of the papers presented at a symposium organized by the British Ecological Society at Oxford in 1959, a meeting convened to bring together research workers in the fields of taxonomy, evolution, genetics, physiology, and ecology of weeds. Although of special interest to the ecologist, this book will undoubtedly be of value to the applied biologist, and should prove useful to the worker in weed control.

The topics covered are diverse, and include well documented contributions on the history of weeds in Britain; dormancy in weed seeds; the spread of weeds by crop seeds; plant competition; the ecology of weeds; toxin production by couch-grass; the comparative life histories of creeping thistle and coltsfoot; and the germination and early establishment of the plantains. Twenty-four papers are given, and Dr Harper's introduction to the volume forms a concise summary of the aim and scope of the symposium.

D. S. C. ERSKINE

PLANT PATHOLOGY

Plant Pathology, *Vol. II*, The Pathogen, *edited by J. G. Horsfall and A. E. Dimond. Pp. xiv+715. Academic Press Inc., New York.* 1960. *$22.*

This volume, the second of three in the series, discusses the antecedents of disease, how disease originates, and, in short, what causes disease. There are chapters on, among other subjects, the pathogen; the nature, origin, and evolution of parasitism; the multiplication and inactivation of viruses; the reproduction of bacteria, actinomycetes, and fungi; spore germination; the breaching of host barriers by mechanical and chemical means; fungitoxicity and fungicidal chemistry; and nematocides.

Each author is a specialist in his own field, and the style is very readable throughout. It is impossible for a present-day plant pathologist to be familiar with advances in all the aspects of his subject, but this book will give him a comprehensive summary of some. C. C. V. BATTS

PHARMACOLOGY

Introduction to Pharmacology, *by J. J. Lewis. Pp. xii + 826. E. & S. Livingstone Ltd, Edinburgh.* 1960. 55*s. net.*

Pharmacology is a troublesome subject because it can be approached from two quite different directions, from that of chemistry and that of biology. The author of this book has approached it from the chemical side, and for the chemist this is an admirable book. For the biologist, and therefore for the medical student, it is, understandably, less suitable. The section on the fate of drugs after absorption, dealing with the chemical changes they undergo, is interesting, informative, and concise; but, on the other hand, the section on the sympathomimetic amines and their physiological properties is out of date.

The chemical emphasis is constantly seen throughout the book. In describing the corticosteroids the author has been fascinated by the new compounds that have been recently introduced and that have shown steadily increasing potency. He has, however, nothing to say about the function of aldosterone, except to mention it in one figure as a very potent minerocorticoid.

The book is intended for medical students; it is to be feared that it will appeal strongly only to the occasional one who has a flair for chemistry.

J. H. BURN

PHARMACY

Bentley and Driver's Textbook of Pharmaceutical Chemistry (*seventh edition*), *revised by J. E. Driver. Pp. ix + 728. Oxford University Press, London.* 1960. 63*s. net.*

During the thirty-five years that have passed since the first edition of this book appeared, professional pharmacy has entirely changed, from a craft, modified by introduction of the basic sciences, to a full academic discipline based on the application of the basic sciences to modern pharmaceutical techniques. The book attempts the impossible: the boundaries of relevant knowledge have been so far extended that it would need many volumes to cover the field.

The new edition is vastly superior to its predecessors, and it is only fair to say that the impossible task has been attempted with some success. Part I covers analytical methods, but many chapters are too short to be of use. Part II, on inorganic chemistry, introduces two new chapters on atomic nuclei and radioactivity, and on periodicity and valency, that are as good as they can be in relation to the space allowed, but would have been much improved had it been possible to include the basic knowledge that is necessary to predict the types of bonds present in inorganic compounds. It is a pity that the study of the modern aspects of inorganic chemistry has not been taken further.

Two-thirds of the book (Part III) is devoted to organic chemistry, and has been extensively revised. Too little attention has been paid to the fundamental roles of inductive, mesomeric, and tautomeric effects, with the result that the student may well be confused.

The factual matter concerning medicinal organic compounds is very well done and mainly up to date; it would be carping to mention certain details with which one did not agree. On the other hand, it is a matter of regret that the fundamentals such as ionization and factors influencing drug action are not discussed at all. Nevertheless, the book would form a valuable addition to the library of anyone interested in pharmaceutical chemistry.

W. H. LINNELL

HISTORY OF SCIENCE

A History of Greek Fire and Gunpowder, *by J. R. Partington. Pp. xvi + 381. W. Heffer & Sons Ltd, Cambridge.* 1960. 70*s. net.*

Professor Partington has made a magnificent contribution to science and to history by bringing his vast knowledge of chemistry to bear on the story of firearms, in the widest sense of the word, from their first appearance into modern times. The range of his inquiry stretches from Western Europe to China, and he has studied all the available sources. Only trained chemists are fitted to dispute his conclusions. Lay historians will be particularly interested by his convincing analysis of Greek Fire and of the part played in it by petroleum, and by his estimate of the role of the Arabs in the development of gunpowder. Apart from some unimportant errors over dates and names and some questionable historical statements, his scholarship is as meticulous as it is wide. One or two of the translations that he uses could be criticized, and he is over-scrupulous in mentioning every possible commentary on his original sources. The subject also raises economic problems that need fuller discussion. But his book will long remain the essential and definitive compendium of information about the use of chemical substances in warfare in past ages. S. RUNCIMAN

SCIENCE IN WARTIME

The Sciences were never at War, *by Sir Gavin de Beer. Pp. xv + 279. Thomas Nelson & Sons Ltd, London.* 1960. 30*s. net.*

Edward Jenner wrote to the *Institut National* of France, in about 1803, a letter containing the sentence 'The Sciences are never at war'; and Sir Gavin de Beer, who is equally at home in English and French culture and letters, has adapted these words as the title for his book. This is concerned with the relationship between English and French men of science from the early days of the Royal Society to the fall of Napoleon. During this period the two countries were at war for an aggregate of nearly sixty years; yet, as the book clearly demonstrates, there was always free and cordial communication between the men of science, culminating in the celebrated visit of Sir Humphry Davy to France, by special permission of Napoleon, in 1813, when he was most hospitably entertained.

The book consists mainly of letters written by celebrated scientific figures, such as Réaumur, Sir Joseph Banks, Delambre, and Jenner, as well as by men of less note, concerning the scientific relationship of the two countries during periods of war, with sufficient felicitous comment to give the reader the contemporary background. Of particular interest is the period of the Napoleonic wars, when the efforts of Sir Joseph Banks played so considerable a part in maintaining friendly contact between the scientists of the two countries. Most of the letters and documents have never been printed before. Translations are provided of all the letters written in French. The book is a valuable contribution to an aspect of the history of science that has not been stressed before. E. N. DA C. ANDRADE

HENRY CAVENDISH

Henry Cavendish: His Life and Scientific Work, *by A. J. Berry. Pp.* 208. *Hutchinson, London.* 1960. 35*s. net.*

This may perhaps be considered Mr Berry's best book; he has performed a useful service by portraying the full extent of Cavendish's amazingly precise scientific work, much of which was not published during his lifetime. The 'Life', however, is little more than a post-mortem examination, as is implied by the heading 'Ancestry and personal characteristics'. A sketch of contemporary developments is then given as an introduction to chapters on Cavendish's researches on general chemistry, dynamical subjects, electricity, heat, meteorology, and the composition of water.

Though useful and instructive for the general reader and the working scientist, the book cannot be unreservedly recommended to students of the history of science. In one place the author betrays his attitude by dismissing a topic as being 'only of historical importance'. What are we to conclude about the remainder? With Cavendish there is no need to exaggerate, such as by calling him the founder of water analysis, or by modernizing the language of his thought—he did not give 'a clear exposition of the principle of reciprocal proportions'. The book is well produced but spoilt by misprints and expressions such as 'obtained *approximately* the correct values' (author's italics). F. W. GIBBS

ROYAL SOCIETY

A Brief History of the Royal Society, *by E. N. da C. Andrade. Pp.* 28. *The Royal Society, London.* 1960. 10*s.* 6*d. net.*

In this short book Professor Andrade relates the history of the Royal Society from its earliest 'prehistoric' meetings in London in 1645 and its formal institution on 28th November 1660 to the presidencies of Banks and of Davy, and then to the more recent and more familiar half-century of 'J. J.', Rutherford, Sherrington, and Hinshelwood. There is much about the Society's publications, about the many duties that it discharges, about its independence, about its international outlook, about its rooms and its treasures, and about the many great names that are included in its illustrious company.

Professor Andrade has here composed a lively account of the Royal Society, and of its work and its functions, as well as of its varying fortunes through three centuries, interspersed with much valuable historical information conveyed with sound judgment and occasionally with shrewd comment, all based on a deep scholarly knowledge of his theme. The reproductions are excellent. D. MCKIE

The Royal Society: its Origins and Founders, *edited by Sir Harold Hartley. Pp.* 275. *The Royal Society, London.* 1960. 35*s. net.*

The Tercentenary of the Royal Society in July 1960 was marked by a great gathering in London of representatives of the world's principal centres of scientific research. This memorable occasion prompted a wealth of tributes, both written and spoken, in many of which the origins and history of the Society were authoritatively considered. Such tributes contain much of interest and value to the historian, but naturally special importance attaches to an historical work compiled by the Society itself; this book certainly does justice to a great occasion. As its title indicates, it is not a complete history but, very fittingly, is devoted to the early days. In a most scholarly and elegantly written first chapter Douglas McKie describes the circumstances, intellectual and political, that led to the famous meeting at Gresham College on 28th November 1660, at which the Society was formally constituted. An interesting feature of the chapter is a critical analysis of the justification for identifying Boyle's 'Invisible College' with the group of philosophers from whose informal meetings the Society grew. Although this identification has been accepted for over two centuries there are now considerable doubts about its validity; Boyle may have been referring to some quite different group that cannot now be identified.

This introductory chapter is followed by a series of biographical sketches, twenty-two in all, of the twelve founder members of the Society and some of those who played a leading part in establishing it. Where available, there is a portrait of the subject. They include Charles II (E. S. de Beer); John Wallis (J. F. Scott); William Ball (A. Armitage); Henry Oldenburg (R. K. Bluhm); and Sir Robert Moray (D. C. Martin). In a short epilogue the Editor discusses the Society's contributions to knowledge, to men's ways of thinking, and to the English language.

This book is not only a splendid memento of a great occasion but one of lasting value. Sir Harold Hartley has clearly taken great pains over its preparation and he and his distinguished collaborators deserve high praise for the result.

TREVOR I. WILLIAMS

HISTORY OF TECHNOLOGY

A Short History of Technology from Earliest Times to A.D. 1900, *by T. K. Derry and Trevor I. Williams. Pp. xviii* + 782. *Clarendon Press, Oxford.* 1960. 38*s. net.*

In recent times there has been a strong movement away from the traditional expression of history in political terms, and both social and economic factors have been given more weight. The upheavals of the twentieth century have now laid bare the great importance of technology. It is plain that the lot of man has been revolutionized by the application of science to agriculture, medicine materials, power, and communications. Warfare and power politics have become dominated by technological developments.

It is therefore most important that a history of technology should have appeared in which the quickening rate of these changes can be studied. The book comes from the same stable as the large five-volume work which appeared two years ago (a "History os Technology," edited by Charles Singer, E. J. Holmyard, A. R. Hall, and Trevor I. Williams). Its attractive style and illustrations will please the general reader, and the wealth of information which it contains will be of particular value to students of history and of technology. The great connections between technology and general history are firmly established; but the book is full of charming and human detail, and it never becomes portentous. This excellent work fills a real need.

PATRICK LINSTEAD

Short notices of books

(These notices are descriptive rather than critical and are designed to give a general indication of the nature and scope of the books.)

An Introduction to Linear Programming and the Theory of Games, *by S. Vajda. Pp.* 76. *John Wiley & Sons Inc., New York; Methuen & Co. Ltd, London.* 1960. 9*s.* 6*d. net.*

What is effectively a new branch of science, operational research, has been developed during and since World War II. This book, which is the amplified text of a series of lectures, deals with two mathematical techniques that are fundamental to operational research: there are chapters on the transportation problem; the concept of duality; the fundamental concepts of the theory of games; non-zero-sum games; and more-person games. It is intended to serve as an introduction to the more specialized texts, and it avoids the use of advanced mathematics.

Russian Chemical Reviews. *No.* 1, *edited by J. N. Agar, R. H. Prince, and A. R. Katritzky. Pp.* 51. *The Chemical Society, London.* £12 *net p.a.*

This is a translation of the Russian journal Успехи Химии and is published in monthly parts that correspond to the Russian original, which is edited by V. V. Korshak. The five or six articles in each issue review recent Russian or, occasionally, Chinese work; articles from other East European countries are not translated, nor are those that are translated from other languages. Papers in the first issue of the translation deal, among other topics, with the chemical action of ultrasonic waves on macromolecules (I. E. El'piner), the hydrides of the rare-earth metals (V. I. Mikheeva and M. E. Kost), and the chemistry of quinuclidine derivatives (M. V. Rubtsov, E. E. Mikhlina, and L. N. Yakhontov).

An Introduction to Physical Chemistry for Biologists and Medical Students, *by H. R. Kruyt and J. T. G. Overbeek (translated by A. J. Mee, in collaboration with J. E. Spice). Pp.* ix + 197. *William Heinemann Ltd, London.* 1960. 25*s. net.*

The emphasis of this book is on colloid science, and, broadly speaking, it deals only with those aspects of physical chemistry that are necessary for understanding colloid science. These aspects include osmotic pressure; reaction velocity; and electrokinetic phenomena. The last third of the book is devoted to colloid science itself.

Handbuch der Papierchromatographie, *Vol. II, by I. M. Hais and K. Macek. Pp.* xxiv + 726. *Gustav Fischer Verlag, Jena,* 1960. *DM* 44.

The first volume of this handbook contained the text: this one contains the bibliography and indexes. There are 10 290 references, subdivided into small groups, dealing with paper chromatography as applied to a very wide variety of substances.

Elements of Ion Exchange, *by R. Kunin. Pp.* ix + 164. *Reinhold Publishing Corporation, New York; Chapman and Hall Ltd, London.* 1960. 46*s. net.*

The intention of this book is to provide a basic understanding of ion-exchange techniques for those with little theoretical background in chemistry. The subjects covered include the structure and synthesis of ion-exchange materials, general principles of ion-exchange applications, and ion-exchange in hydrometallurgy and related fields.

The Effects of Pollution on Living Material, *edited by W. B. Yapp. Pp.* xii + 154. *The Institute of Biology, London.* 1959. 25*s. net.*

This, the eighth of the symposia of the Institute of Biology, is the account of a meeting held in London in 1958. Some of the papers are concerned with local problems, such as that of the general condition of the rivers of Britain; but most deal with larger issues, such as the effects of air pollution on plant growth and on man, the uptake of fission products by plants, the relation between pollution and the abundance of animals in estuaries, and fluorosis in farm animals.

Methods of Biochemical Analysis, *Vol. VIII, edited by D. Glick. Pp.* ix + 400. *Interscience Publishers Inc., New York; Interscience Publishers Ltd, London.* 1960. 75*s. net.*

The editor of this series considers that there is a need for reviews concerned with techniques and methods as well as those devoted to progress in the various fields of science. The subjects of the papers in this volume include qualitative and quantitative determination of the fatty acids by gas-liquid chromatography, the measurement of luciferin and luciferase, the isolation and determination of neuraminic acids, and the determination of porphyrins in biological materials.

Plant Marvels in Miniature; a Photographic Study, *by C. Postma. Pp.* 173. *George G. Harrap & Co. Ltd, London.* 1960. 45*s. net.*

The photographs in this book are arranged in series, so as to show, for example, roots, the parts of a spiderwort, and leaf buds, under increasing magnification, up to, in some cases, three thousand times. The photographs are large, and the aim is to provide aesthetically satisfying pictures together with a scientific descriptive text.

Plant Viruses (*third edition*), *by K. M. Smith. Pp.* xii + 209. *Methuen & Co. Ltd, London.* 1960. 16*s.* 6*d. net.*

The first of the two main sections into which this book is divided deals with the basic principles of plant virology and the means by which a knowledge of these principles has been attained. The second part gives a concise account of the practical methods of study, although no attempt is made to give detailed accounts of such specialized and complicated techniques as those necessary in the electron microscopy of viruses. The book is intended for the student with no previous knowledge of plant viruses.

Oysters, *by C. M. Yonge. Pp.* xiv + 209. *Collins, London.* 1960. 21*s. net.*

This book aims at providing a balanced account of oysters, and the chapters cover the structure, the mode of functioning, and the habits of oysters; their use as food; and their cultivation, giving a historical background to the modern techniques.

Fats and Oils (*second edition*), *by H. Kirschenbauer. Pp.* vi + 240. *Reinhold Publishing Corp., New York; Chapman and Hall Ltd, London.* 1960. 56*s. net.*

The author has aimed, when revising the first edition, at keeping the book compact; at the same time he attempts to include the latest information on the chemical structure, methods of processing, and use of fats and oils, both animal and vegetable. Among the subjects covered are autoxidation, rancidity, cholesterol in diet, selective hydrogenation, and sequestering agents.